

GENERAL METALLURGY



MIR PUBLISHERS

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ОБЩАЯ МЕТАЛЛУРГИЯ

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Contents

Part One

AN INTRODUCTION TO METALLURGY

Chapter	I. FUNDAMENTALS OF METALLURGY	11
	1. Classification of Metals	11
	2. Sources of Metals	14
	3. Extraction of Metals from Ores	16
Chapter	II. THE PREPARATION OF ORES	20
	4. Comminution of Ores	20
	5. Sizing	26
	6. Ore Dressing—Scope and Methods	31
	7. Flotation	32
	8. Gravity Concentration	36
	9. Magnetic Separation	39
	10. Dewatering	41

Part Two

THE METALLURGY OF IRON

Chapter	III. IRON AND ITS COMMERCIAL ALLOYS	49
	11. General	49
Chapter	IV. THE METALLURGY OF PIG IRON	52
	12. Iron Ores	52
	13. Preliminary Treatment of Iron Ores	53
	14. Blast-furnace Fuel	56
	15. Fluxes	57
	16. Description of a Modern Blast Furnace	57
	17. Accessories to the Blast Furnace	64
	18. Cleaning of Blast-furnace Gas	66
	19. Blast-furnace Reactions	71
	20. Products of Blast-furnace Operation	80
	21. Blast-furnace Working	84
	22. Efficiency of the Blast Furnace	85

Chapter	V. THE MANUFACTURE OF STEEL	87
A. The	Bessemer Processes	87
	23. The Acid Bessemer Process	87
	24. The Basic Bessemer (Thomas-Gilchrist) Process	92
	25. Finishing Additions	95
	26. Converter Construction	96
	27. Side-blown Converter Practice	97
	28. Oxygen Steelmaking	99
	29. Uses for Converter Steel	101
B. The	Open-hearth Processes	102
	30. Principles of the Processes	102
	31. The Open-hearth Furnace	104
	32. Open-hearth Fuels	108
	33. The Charge for the Open-hearth Furnace	110
	34. The Basic Open-hearth Process	111
	35. Deoxidation of Open-hearth Steel	116
	36. Rimming Steel	117
	37. The Acid Open-hearth Process	117
	38. Quality, Properties and Uses of Acid Open-hearth Steel	118
	39. Economics of the Open-hearth Process	119
	40. Oxygen Enrichment of the Open-hearth Furnace Blast	119
	41. Automatic Control of the Open-hearth Furnace	120
C. The	Electric Processes	121
	42. The Direct or Arc-resistance Furnace	122
	43. Arc-furnace Processes	124
	44. Economics of the Arc-resistance Furnace Process	127
	45. The Induction Furnace	128
	46. Duplex Processes	128
	47. Utilisation of Complex Ores	129
	48. Ingot Production	129

Part Three

THE METALLURGY OF HEAVY NON-FERROUS METALS

Chapter	VI. THE METALLURGY OF COPPER	134
	49. General	134
	50. Sources of Copper	136
	51. Production of Copper from Ores and Concentrates	138
	52. Matte Smelting from Ores	148

53. Matte Smelting from Concentrates	157
54. Converting	169
55. Scrap (Secondary) Copper	175
56. The Refining of Blister Copper	176

Chapter VII. THE METALLURGY OF NICKEL 191

57. General	191
58. Sources of Nickel	192
59. A General Outline of the Processes	193
60. Commercial Processes for Oxide Nickel Ores	198
61. Commercial Processes for Sulphide Nickel Ores	206
62. Electrolytic Nickel Refining	217
63. Cobalt Manufacture	221

Chapter VIII. THE METALLURGY OF LEAD 225

64. General	225
65. Sources of Lead	227
66. The Art of Lead Ore Smelting	229
67. Blast Roasting of Lead Concentrates	233
68. Blast-furnace Smelting of Lead Bullion	238
69. Refining of Lead Bullion	249
70. Extraction of Calcium and Other Metals from Lead Concentrates	269

Chapter IX. THE METALLURGY OF TIN 270

71. General	270
72. Tin Ores	271
73. Preparing the Ore for Smelting	272
74. Extraction of Tin	275
75. Primary Smelting	277
76. Resmelting of the First-run Slag	282
77. Tin Refining by Heat Treatment	283
78. Electrolytic Refining of Tin	288
79. Extraction of Other Metals from Tin Ores	289

Chapter X. THE METALLURGY OF ZINC 290

80. General	290
81. Zinc Ores	291
82. General Principles of Zinc Extraction	292
83. Roasting of Zinc Concentrates	294
84. Leaching of Roasted Zinc Concentrates	301

85. Purification of Neutral Zinc Sulphate Solution . . .	308
86. The Electrolysis of Zinc Sulphate Solution	311
87. Melting of Cathode Zinc	318
88. Economics of Zinc Hydrometallurgy	319
89. Horizontal Retort Practice	321
90. The Vertical Retort Process	330
91. Zinc Distillation in Electric Furnaces	332
92. The Production of Zinc in a Blast Furnace	333
93. The Refining of Slab Zinc	335
94. Recovery of Scrap Zinc	341
95. Extraction of Other Metals from Zinc Concentrates	343

Part Four

THE METALLURGY OF THE PRECIOUS METALS

Chapter	XI. THE METALLURGY OF GOLD	347
	96. General	347
	97. Sources of Gold	348
	98. Methods of Gold Recovery	349
	99. Gravity Concentration	351
	100. Amalgamation	356
	101. Cyanidation	361
	102. Gold Precipitation from Cyanide Solutions . . .	370
	103. Typical Flow-sheets	374
Chapter	XII. AN OUTLINE OF SILVER	380
	104. Properties and Uses	380
	105. Sources and Production of Silver	381
Chapter	XIII. A BRIEF OUTLINE OF THE PLATINUM GROUP . . .	382
	106. Properties and Uses	382
	107. Sources of the Platinum Metals	384
Chapter	XIV. REFINING OF GOLD AND SILVER BULLION . . .	385
	108. General	385
	109. Silver Refining by Electrolysis	386
	110. Gold Refining by Electrolysis	387
	111. Refining of the Platinum Metals	388

Part Five

THE METALLURGY OF THE LIGHT-WEIGHT METALS

Chapter	XV. THE METALLURGY OF ALUMINIUM	391
	112. General	391
	113. Sources of Aluminium	394
	114. Historical Survey	396
Chapter	XVI. THE PREPARATION OF ALUMINA, CRYOLITE AND CARBON ELECTRODES	398
	115. Properties of Alumina and a General Outline of Its Preparation	398
	116. The Bayer Process of Alumina Preparation . .	400
	117. The Deville-Pechiney (Le Chatelier-Morin) Process of Alumina Preparation	411
	118. Other Processes of Alumina Preparation	422
	119. The Preparation of Cryolite	424
	120. The Manufacture of Carbon Electrodes and Anode Material	427
Chapter	XVII. THE PRODUCTION OF METALLIC ALUMINIUM . .	430
	121. The Composition and Properties of the Bath . .	430
	122. The Anode Effect	434
	123. Minor Effects at the Cathode and in the Electrolyte	436
	124. The Efficiency of the Electrolytic Process . . .	438
	125. Improvements in Reduction Cell Design	441
	126. Aluminium Refining	452
	127. Auxiliary Operations in the Production of Electro- lytic Aluminium	459
	128. Economics of Aluminium Production	461
	129. Thermal Processes of Aluminium-alloy Production	462
	130. Recovery of Other Values from Aluminium Ores	466
Chapter	XVIII. THE METALLURGY OF MAGNESIUM	469
	131. Magnesium and Its Alloys—a General Outline	469
	132. Sources of Magnesium	470
	133. Production of Magnesium	472
	134. Preparation of Magnesium Chloride for Electrolysis	472
	135. Electrolytic Production of Magnesium	479
	136. Cell Design and Practical Electrolysis	485

137. Refining and Casting of Magnesium	492
138. Economics of Electrolytic Magnesium Production.	495
139. Magnesium Reduction Processes	496

Part Six

THE METALLURGY OF REFRACTORY METALS

Chapter XIX. THE METALLURGY OF TUNGSTEN	504
140. General	504
141. Sources of Tungsten	506
142. Treatment of Tungsten Concentrates	507
143. The Production of Tungsten Metal Powder	515
144. The Manufacture of Ductile Tungsten	517
Chapter XX. THE METALLURGY OF MOLYBDENUM	521
145. General	521
146. Sources of Molybdenum	522
147. Conversion of Molybdenum Concentrates	522
148. Molybdenum Metal Powder and Ductile Molybdenum	528
149. Recovery of Other Values from Molybdenum Ores	530
Chapter XXI. THE METALLURGY OF TITANIUM	531
150. General	531
151. Sources of Titanium	532
152. Treatment of Ilmenite Concentrates	533
153. The Production of Titanium Tetrachloride	533
154. The Production of Titanium Metal	536
Appendix I	542
Appendix II	547
Subject Index	548

Part One

AN INTRODUCTION TO METALLURGY

Chapter I

FUNDAMENTALS OF METALLURGY

1. Classification of Metals

Lomonosov classed as metals "...lustrous bodies which can be forged". However, physical properties, such as lustre, malleability, high electrical and thermal conductivity, are not a sufficient basis for a clear delineation to be made between metals and non-metals. Nor are chemical properties good enough for this purpose sometimes, since many elements are amphoteric, i.e., capable of reacting as both acids and bases.

Elements are often classed as metals by tradition, on the basis of their production and uses; thus, we have a total of eighty traditional metals.

Mendeleyev's Periodic Table gives a comprehensive account of the properties of metals, but it is unable to show their relative economic value. Therefore, a commercial classification has come into being. Though not strictly scientific, it has given rise to a widely used terminology.

The commercial classification of metals (Table 1), above all, groups the metals into *ferrous* and *non-ferrous*. In the first category it places iron which is used in a great variety of alloys with carbon known

Table 1

Commercial Classification of Metals

Group	Elements
Ferrous metals	Iron and its alloys
Non-ferrous metals:	
(a) heavy	Cu, Ni, Pb, Zn, Sn
(b) light	Al, Mg, Be, Li, Ba, Ca, Sr, K, Na, Rb, Cs
(c) noble (or precious)	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd
(d) minor (or secondary)	As, Sb, Bi, Cd, Hg, Co
(e) refractory	W, Mo, Ta, Nb, Ti, Zr, V
(f) scattered	Ge, In, Ga, Tl, Hf, Re
(g) radioactive	Ra, Ac, Th, Pa, U and elements 93-102
(h) rare-earth	Y, La, Ce, Nd, Pr, Sm, Gd, Dy, Er, Yb, Pm, Eu, Tb, Ho, Tu, Lu, Sc
(i) ferroalloy*	Cr, Mn

Note: Sometimes the term "rare" is applied to groups (e), (f), (g) and (h) collectively.

* Chromium and manganese, mainly used as alloying elements in cast irons and steels, are often classed as ferrous metals. Now that these metals have come to be used in elemental form it will be more appropriate to class them as non-ferrous metals. According to Pazukhin, they should be termed ferroalloy metals.

as irons and steels. Thereby, the exceptional role of iron as the main structural material in engineering is stressed, which actually is the case, judging from the scope of iron production and consumption.

The non-ferrous metals are divided into *heavy*, such as copper, nickel, lead, zinc and tin; and *light* metals among which the most important commercially is aluminium. The specific gravities of the heavy non-ferrous metals range between 7 and 11 (in round figures) and of the light metals below 4. Apart from aluminium, the light metals include magnesium, barium, calcium, strontium, beryllium, lithium, potassium, sodium, rubidium and cesium.

A separate group of *noble* or *precious* metals includes gold and silver. The group owes its name to the fact that gold withstands the action of strong mineral acids and that gold and silver have been used as the monetary standards for centuries. This group also includes platinum and its associates: palladium, rhodium, iridium, ruthenium and osmium.

Bismuth, cadmium, arsenic, antimony and mercury are used in the world in almost equal amounts (10 to 20 thousand tons a

year). They are called *minor* metals. It seems logical to include cobalt in this group.

Tungsten, molybdenum, titanium, vanadium, zirconium, tantalum and niobium, although mainly used as alloying elements in steel, also have uses of their own. The melting points of these metals are above 1650°C. for which reason they are called *refractory* metals.

The *scattered* metals (germanium, indium, gallium, thallium, hafnium and rhenium), as the name of the group implies, are distributed in extremely minute quantities in the earth's crust. They

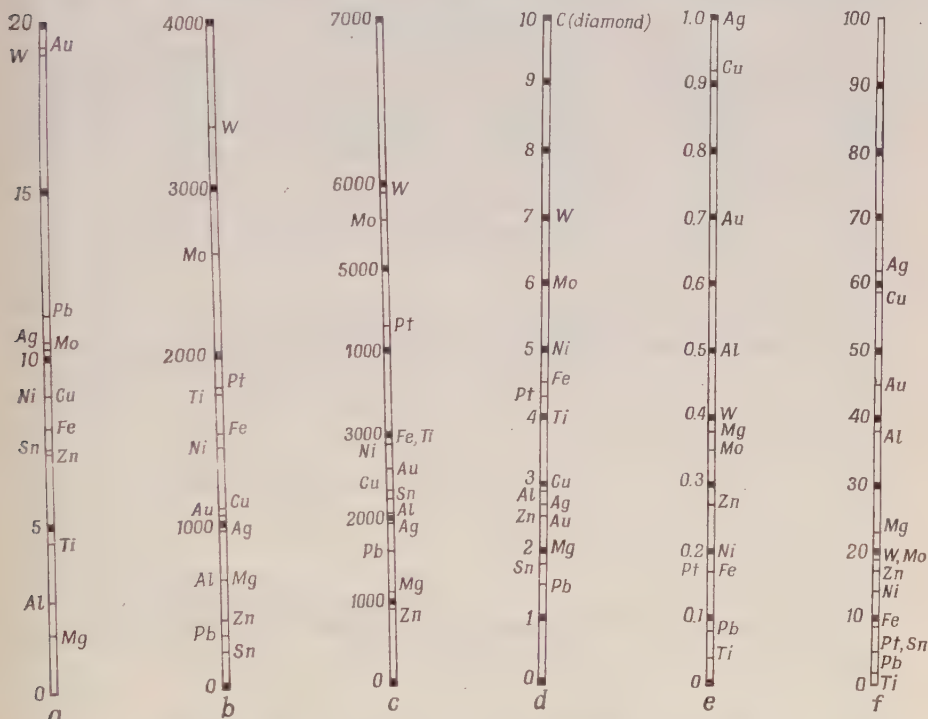


Fig. 1. Principal physical properties of some metals:

(a) density at 20°C, g/cu cm; (b) melting point, deg. C; (c) boiling point, deg. C; (d) hardness on decimal scale; (e) electrical conductivity at 20°C, ohm⁻¹-cm⁻¹; (f) thermal conductivity in the temperature range 0-100°C, cal/cm-sec-deg (× 10⁻⁴)

have no ores of their own, and their minerals (except for germanium) are so scarce as to offer little promise as a source of production. On the other hand, these metals are found in the minerals of other metals.

What is called the *radioactive* group of metals today came to be considered as such during the early attempts to use nuclear power

and uranium as its chief fuel. Now, this group includes thorium, radium, protactinium and man-made transuranic elements.

The *rare-earth* group includes fourteen elements of the original Periodic Table and the elements lanthanum, yttrium and scandium.

The physical properties of metals depend to a high degree on their purity and their history prior to measurements. Their principal properties are roughly outlined in Fig. 1 and will be further dealt with elsewhere in the book.

2. Sources of Metals

Metals are mostly obtained from bodies of material occurring in the earth's crust and called *ores*. Ore may be defined as a metal-bearing mineral or an aggregate of such minerals, containing a large enough proportion of the metal as to permit, at a given stage of mining art, its extraction at a profit.

The lithosphere, or the earth's crust to a depth of about 16 km, contains an average of 46.59 per cent oxygen, 27.72 per cent silicon, and the remainder (25.69 per cent) other elements, including all metals. The percentage abundance of the metals in the earth's crust is presented in Table 2.

The mineral or minerals making up an ore are chemical compounds occurring in nature. The valuable mineral contained in an ore is an *ore mineral*. The other minerals contained in the mixture, which ordinarily are waste material, constitute the *gangue* of the ore.

Cheaper methods of extraction are continually developed which show a profit in recovery of metals from ores too lean to be treated by previous methods. At the turn of the present century, it was considered unprofitable to extract lead from ores containing less than 1 per cent of this metal, and such ores were not classed as ores in the technical sense of the word at all. At present, lead is extracted at a profit from ores containing as little as 0.3 per cent Pb.

Ore bodies are local concentrations of one or several chemical elements. The proportion of the metals in them is considerably higher than their percentage abundance in the earth's crust. The proportion of iron in ores may often be as high as 50-60 per cent and that of copper 1-2 per cent. The metals differ greatly in their concentration in ore bodies. While tin and germanium show approximately the same abundance in the earth's crust, the presence of 0.01 per cent Sn in an ore is considered very low, while 0.01 per cent Ge is a bonanza.

Usually ores are designated on the basis of the principal component of the ore mineral, accounting for its commercial value, such as a copper ore, an iron ore, etc. It should be noted, however, that

Table 2

Average Abundance of Metals in the Earth's Crust
(per cent by weight)

1-10	10-1-1	$\frac{10^{-2}}{10^{-1}}$	10-3-10-2	10-4-10-3	10-5-10-4	10-6-10-5	10-7-10-6	10-10-10-9
Al 7.45	Ti 0.60	Ba 0.05	Rb 8×10^{-3}	Sc 6×10^{-4}	Sb 5×10^{-5}	Hg 5×10^{-6}	Au 5×10^{-7}	Ra 2×10^{-10}
Fe 4.20	Mn 0.10	Sr 0.035	Li 5×10^{-3}	As 5×10^{-4}	Nb 3.2×10^{-5}	Pd 5×10^{-6}	Re 10^{-7}	
Ca 3.25		Cr 0.03	Y 5×10^{-3}	U 4×10^{-4}	Ta 2.4×10^{-5}	Ru 5×10^{-6}		
Na 2.40		Zr 0.025	Sn 8×10^{-3}	Be 4×10^{-4}	Pt 5×10^{-5}	Os 5×10^{-6}		
K 2.35		V 0.02	Co 2×10^{-3}	Cd 5×10^{-4}	Ag 10^{-5}	Rh 10^{-6}		
Mo 2.35		Ni 0.02	Th 10^{-3}	Hf 4×10^{-4}	Tl 10^{-5}	Se 10^{-6}		
		Zn 0.02	Pb 1.6×10^{-3}	Ge 10^{-4}	Bi 10^{-5}			
		Cu 0.01	W 7×10^{-3}	Ga 10^{-4}	In 10^{-5}			
		R.E. 0.01	Mo 10^{-3}					
			Cs 10^{-3}					

single-component ores are almost non-existent in nature. More often they are associations of two or more ore minerals, which fact is reflected in their designations, such as copper-nickel ores, zinc-lead ores. Yet, composite names of ores which serve as a source of several metals would often be too awkward to use, and such ores are classed on the basis of the prevailing metal.

Ores may be classified according to the compositional type of ore mineral contained. The most important types are the sulphide ores, the native ores, and the oxide ores. In addition to oxides, the latter class may include, under the classification adopted in the Soviet Union, also other oxygen-bearing minerals, such as carbonates, silicates, etc.

Apart from ores, metals may be obtained from what may be called secondary sources: drillings, turnings, sawings, industrial and household scrap, metal-making wastes. Secondary sources play an important role in the fabrication of iron, copper, lead, and aluminium, to name but a few metals.

3. Extraction of Metals from Ores

Before a pure metal can be extracted from its ore, the latter must first be separated from its gangue, the ore mineral decomposed, and the metal separated from the elements with which it may be combined chemically. The physical and chemical methods employed for the purpose are called *metallurgical processes*. A scientific basis for them is furnished by the theory of metallurgical processes.

Some of the gangue may be separated from the ore mineral by using differences in their physical properties: specific gravity, hardness, permeability, electrical conductivity, or difference in adhesion of the mineral surface. Such methods are cheap, and they do not change the chemical composition or state of the ore mineral. They only produce concentrates of the mineral values, however, and not pure metals. Such processes are called *ore dressing* or concentration, and are operations preparatory to the actual extraction of a metal from its ore.

Metallurgical extraction methods are divisible into two groups. One, involving the use of elevated temperatures and changes in the chemical composition of the entire body of ore, is classed as pyrometallurgy. The other, based on the dissolving of the metal sought in aqueous solutions of acids or alkalis and subsequent precipitation, is classed as hydrometallurgy.

In either case, the objective is the division of the ore into two or three phases. Through suitable chemical reactions, the metal sought is concentrated in one of the phases, and the wastes in the other. As a rule, metallurgical treatment consists of several stages,

each stage concentrating the metal ever more, until a pure metal is obtained.

The basic processes of pyrometallurgy are smelting, roasting, and distillation.

Smelting uses temperatures sufficient to melt the metal. The molten material will then separate itself into two or more immiscible liquids according to their specific gravities. There may be reducing, oxidising or liquation smelting, depending on the reaction that underlies the process and results in the formation of a multiphase system. The reader will find practical examples of them elsewhere in the book.

Roasting (or calcination) uses elevated temperatures not sufficiently high to fuse the metal. The reagents employed in roasting may be gases or solids. The objective of roasting is to prepare the material for further treatment. There may be reducing, oxidising, chlorinating, sulphatising and other types of roasting. Standing midway between smelting and roasting is sintering in which the metal sought is partly melted; or, rather, its low-melting component is melted. In cooling, the liquid phase solidifies and binds the particles of the material, thereby turning it into a porous but strong sinter. Sintering is employed to turn a finely divided material into an agglomerate. Sintering may be accompanied by reducing, oxidising or any other type of roasting.

Distillation is a process by which the metal or its chemical compounds are evaporated to liberate them from the non-volatile components of the charge. The vapours of the metal or its compounds are then precipitated in a more or less pure state.

The basic processes of hydrometallurgy are leaching, thickening and precipitation of metals or their compounds from solutions.

Leaching involves the selective solution of some of the components in the ore, most often containing the metal sought, while leaving the gangue undissolved.

In many cases, the temperature of leaching is above the boiling point of the solutions used; then leaching is conducted under pressure in autoclaves which are hermetically sealed thick-walled vessels. In commercial autoclaves, the temperature of leaching may be anywhere from 220 to 260°C.

Sometimes, when the mineral is difficult to decompose, leaching may be preceded by roasting or smelting. This involves no separation of the mineral into phases. An example is provided by the roasting of zinc concentrates or the sintering of bauxites.

The metal sought or its compounds obtained by leaching are precipitated from the solution after it has been separated from the undissolved residue by means of filtering or settling. In elemental form, a metal can be precipitated from a solution either electro-

lytically, as in the case of copper, zinc or nickel, or by cementation according to the reaction



The precipitation of metals from solutions in the form of nearly insoluble chemical compounds resembles the techniques of quantitative analysis. Very often precipitation is accomplished by hydrolysis reactions in which the activity of the ions H^+ and OH^- is mainly changed in the solution. Precipitation also includes the crystallisation of metallic salts by cooling or evaporation.

Prior to precipitation, it is sometimes advantageous to concentrate the solution. This is especially true of lean materials the leached solutions of which are usually diluted or contain large amounts of impurities. Concentration may be accomplished by means of ion exchange, extraction or evaporation.

Ion exchange is based on the ability of an ion exchange material (ion exchange resins) to absorb metallic ions from solutions. The resins absorbing cations are called cationic exchangers, and those absorbing anions are called anionic exchangers. Ion exchange being a reversible process, the ions absorbed by an exchanger can be replaced by other ions in a relatively small volume of water. For this purpose, a simple salt, which may be sodium chloride or nitrate, is dissolved in water and the exchanger is placed there.

Extraction is based on mixing a solution with an organic liquid nearly insoluble in water and a reagent capable of forming with the metal compounds more readily soluble in the organic liquid than in water. Sometimes, the organic (extracting) liquid doubles as the reagent forming soluble compounds. The resulting mixture is allowed to settle and separate itself into two layers, one being water and the other the organic solution. The compounds of the metal usually pass into the organic phase which is separated and the desired compounds are removed by adding a little acid or salt. Several successive stages of extraction usually make it possible to recover the metal selectively and almost fully.

A few words should be added about the theory underlying the metallurgical processes.

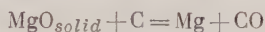
The basis of metallurgy is the chemical reactions brought about in order to decompose ore minerals, to distribute metals between immiscible phases, and to reduce their compounds to metallic form. A clear understanding of the metallurgical processes calls for an assessment of the possibility for a reaction to take place under given conditions, its course and rate, or velocity.

As will be recalled, whether or not a given reaction may take place under prevailing conditions depends on the sign of the change of the standard free energy ΔG . If the change of the standard free

energy is negative, the reaction may proceed spontaneously. The calculation of the standard free energies, treated by thermochemistry, is sometimes too involved for practical use. Therefore, the metallurgist usually resorts to what is called the standard affinity of metals for metalloids, i.e., the strength of the bonds in chemical compounds. Appendix I shows the standard affinity of metals for oxygen and sulphur as a function of temperature. Appendix II contains data on the vapour pressures of some metals and their compounds which sometimes enter in metallurgical calculations.

More accurately the direction of reactions and their equilibrium constants may be determined by the approximate equations given in the two appendices.

As an example, let us determine the temperature necessary for the reduction of magnesium oxide with carbon according to the reaction



As this reaction calls for elevated temperature, we shall use the equation for the temperature range 1376-2500°K (see Appendix I)

$$\begin{aligned}\Delta G &= \Delta G_{\text{CO}} - \Delta G_{\text{MgO}} \\ \Delta G_{\text{CO}} &= -26,700 - 20.95T \\ \Delta G_{\text{MgO}} &= 181,600 - 7.37T \log T + 75.7T \\ \hline \Delta G &= 154,900 + 7.37T \log T - 96.65T\end{aligned}$$

Substituting the limiting values, i.e., 2000 and 3000°K and completing the necessary calculations, we shall obtain:

T ,	°K	2000	2150	2200	2250	2500	3000
t ,	°C	1727	1877	1927	1977	2227	2727
ΔG ,	cal	10,340	120	-3300	-8500	-23,440	-57,890

In other words, the reduction of magnesium oxide by carbon under normal conditions ($P_{\text{Mg}} = P_{\text{CO}} = 1$ atm abs) will begin at about 1900°C.

Reaction rates are a metallurgically vital problem which does not lend itself to any general, albeit approximate evaluation. Any discussion of metallurgical processes from this angle inevitably involves a multitude of kinetic factors which can only be expressed qualitatively. It seems safe, however, to think that in most of the heterogeneous reactions involved in metallurgical processes the controlling factor is diffusion, while the rate of a reaction mainly depends on the area of contact between the phases and temperature. While stressing the importance of kinetics, it should be noted that many reactions, thermodynamically possible, become practically feasible only at temperatures several hundred degrees higher than the expected one. For example, coke will only ignite at 720-730°C, though thermodynamically it can burn under normal conditions.

Chapter II

THE PREPARATION OF ORES

4. Comminution of Ores

Ores come from a mine in lumps measuring up to 1200 to 1500 mm across. For metallurgical treatments, smaller pieces, sometimes very finely divided (less than 0.1 mm across), are required. For this reason, ores are comminuted, i.e., reduced in size, in breakers, crushers and mills. For its operation, breaking, crushing and grinding plant depends on impact, crushing, or attrition.

Each piece of breaking, crushing and grinding equipment will operate efficiently only in the specified range of lump sizes. Comminution consumes much power which increases as the size of the product is decreased. Therefore, the guiding principle in size-reduction practice is "not to crush any more thoroughly than is necessary".

Comminution may involve several stages differing in the size of the feed and of the product:

	Feed size, mm	Product size, mm
Breaking (or primary crushing)	1500-300	300-100
Crushing	300-100	50-10
Fine crushing	50-10	10-2
Grinding	20	0.05 and smaller

Levenson of the U.S.S.R. has suggested the following classification of breaking, crushing and grinding equipment:

(1) Jaw crushers in which the feed is reduced in size periodically between a stationary and a movable jaw plate.

(2) Gyratory and cone crushers in which the feed is reduced in size continuously between two cones, one cone rolling over the inside surface of the other.

(3) Rolls in which the feed is reduced in size between two rolls rotating in opposite direction; the rolls may be smooth, ribbed, or toothed.

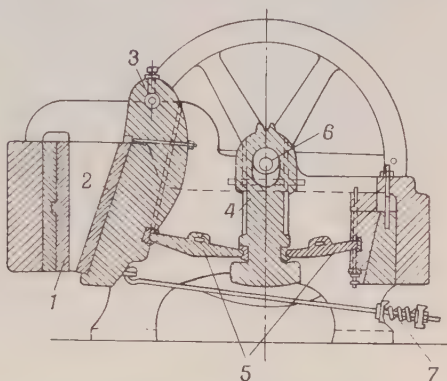
(4) Hammer or rod crushers in which the feed is reduced in size by the impact of falling hammers or rods.

(5) Mullers in which the feed is reduced in size by heavy tyres over a hard circular pan.

(6) Ball mills in which the material is reduced in size by freely falling steel balls or slugs.

Fig. 2 shows a jaw crusher. The feed is crushed between jaws of hard steel. The jaws are wavy on the surface so that the hills on the movable jaw fit into the hollows on the stationary jaw. As the shaft and eccentric rotate, the pitman 4 alternately moves up and down, actuating the toggles 5. When the pitman is at top dead centre, the toggles force the movable jaw against the stationary

Fig. 2. Jaw crusher:
1—stationary jaw; 2—movable jaw; 3—swing-jaw shaft; 4—pitman; 5—toggles; 6—drive shaft and eccentric; 7—opposing spring and tension rod



jaw, and the material between them is crushed. When the opposing spring 7 forces the movable jaw away, the crushed product falls down between the jaws.

Jaw crushers are mostly employed for primary and less for secondary coarse crushing. Their capacity may be as high as 500 tons an hour and their reduction ratio ranges between 4 and 6.

Gyratory crushers, which are available in a variety of makes, are employed for primary, secondary coarse and fine crushing. Their capacity reaches 2100 tons an hour.

Fig. 3 shows a suspended-spindle gyratory crusher. It consists of a fixed crushing surface, in the form of a frustum of an inverted cone (known as concaves), around the axis of which gyrates a movable crushing surface (called the inner crushing head), having the shape of a conical frustum in erect position. The head and concave are clad with hard manganese steel. The top end of the spindle which carries the movable crushing head is suspended from the crusher shell, and its lower end is free to enter the eccentric sleeve driven by an electric motor via a gear transmission. The fixed concave is made fast to the crusher frame.

Fig. 4 shows a secondary (Symons) cone crusher. It differs from the previous type in that the outside crushing surface instead of flaring in from top to bottom flares out. It uses a fixed spindle and has a greater nip angle, for which reason the product is more uniform in size and a greater reduction ratio is attained. The shell

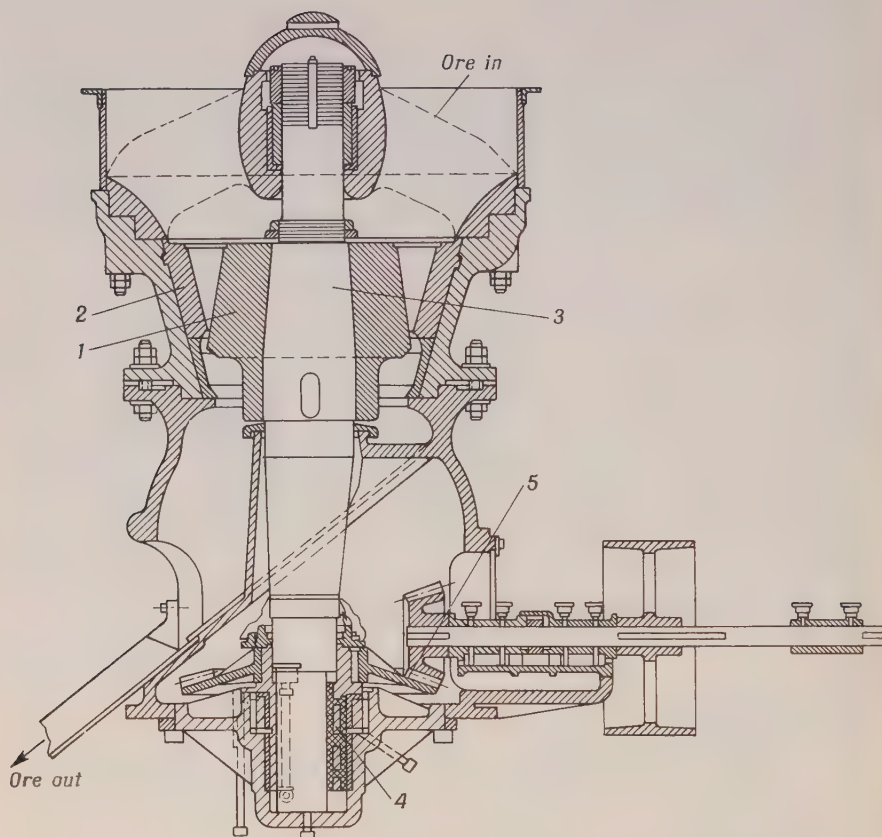


Fig. 3. Gyratory crusher:

1—movable crushing head; 2—fixed concave; 3—spindle; 4—eccentric sleeve; 5—gear transmission

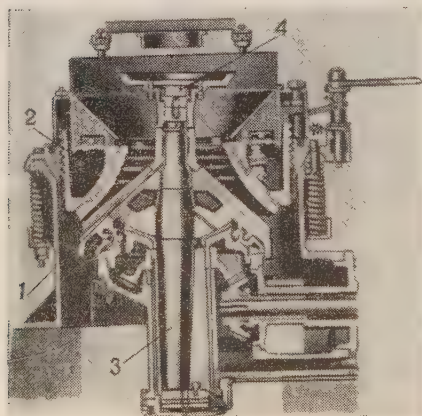


Fig. 4. Symons cone crusher:

1—movable crushing surface; 2—fixed crushing surface; 3—drive shaft; 4—plate feeder

is made up of two halves joined by steel springs as a precaution against breakage, should excessive loads be caused by "tramp" iron.

Rolls (Fig. 5) are usually employed for secondary coarse and fine crushing.

Hammer or beater mills may be used for primary and secondary coarse and fine crushing. In the latter two cases they are called disintegrators and operate on brittle and relatively soft materials.

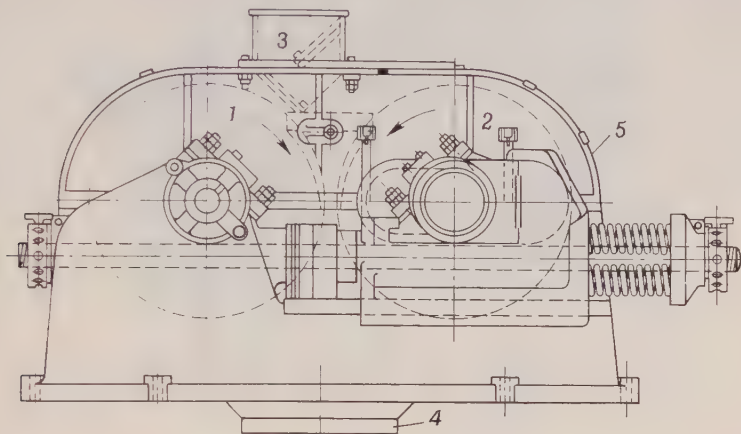


Fig. 5. Rolls:

1, 2—rollers; 3—feed hopper; 4—discharge outlet; 5—shell

Sometimes disintegrators only serve to mix loose materials. In the beater mill whose section is shown in Fig. 6 the central shaft completes 800 to 1000 revolutions every minute. The feed is crushed either by freely falling hammers or bars or due to impact against the shell walls. Fig. 7 shows a disintegrator.

Grinding mills (Fig. 8) are used for finely grinding feed with a particle size of not more than 50 mm across. The feed and steel balls or rods are charged into a horizontal steel drum lined with renewable steel plates. The drum rotates about its axis, the balls or rods are lifted to a height and fall down, reducing the ore lumps in the process. Proper speed has a decisive effect on mill operation. When the speed is too high, the balls or rods will be pressed against the drum by centrifugal force. When the rpm is too low, the balls or rods will roll over the lower portion of the drum, and the grinding will be insufficient, by attrition only.

Mills may use rods, balls or flint pebbles. Flint pebbles are used where it is essential that the product may not be contaminated by the iron of the balls or rods.

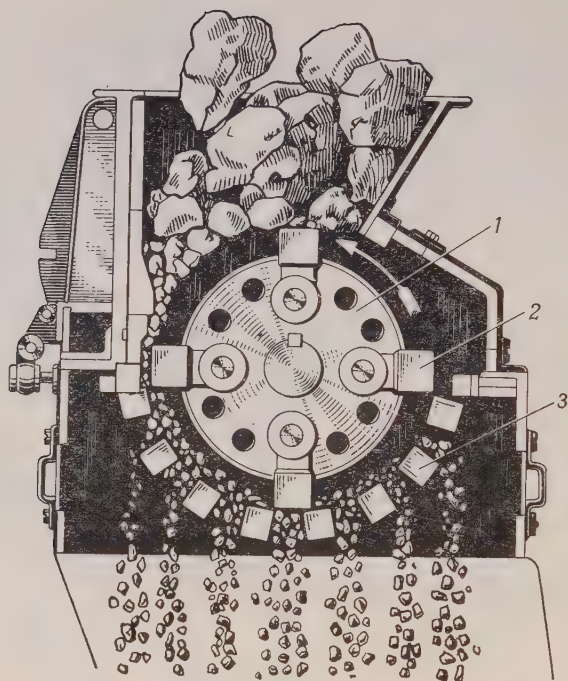


Fig. 6. Beater mill:
1—central shaft; 2—beaters; 3—bar screen

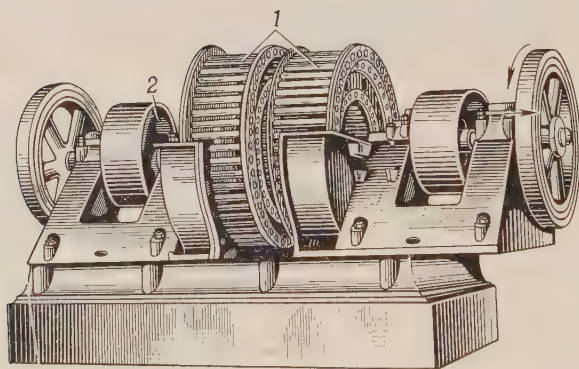


Fig. 7. Disintegrator (with shafts drawn apart and shell partially removed):
1—shafts; 2—shell

Mills may be conical or cylindrical. Cylindrical mills whose length is 3 to 6 times their diameter are called tube-mills.

Fine grinding is usually accomplished in a liquid to prevent rump and dust formation. The mixture of solid particles and liquid (water or solutions) is called the pulp. The density of the pulp is evaluated in terms of the liquid to solid ratio or in per cent of the

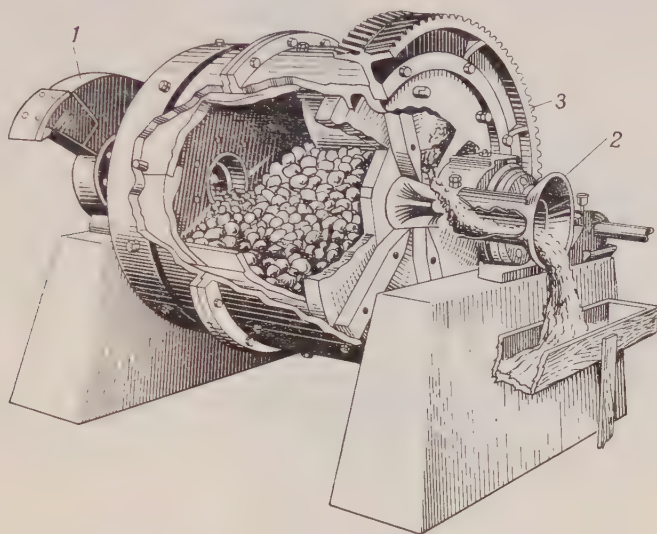


Fig. 8. Ball mill:

1—feeder; 2—hollow trunnion; 3—drive rim

solid material by weight. The pulp reduced in mills usually contains 40 to 75 per cent of the solid material. The ore may be charged either continuously or intermittently. When charged continuously, the ore is fed through an open trunnion at one end and is discharged at the other end.

The current trend is to use mills without any grinding bodies, based on the self-attrition of the charge.

In most cases, mills are run continuously. The ore and water are fed through a hollow trunnion at one end, and the reduced pulp is discharged at the other. The fineness of grinding may be adjusted by varying the feed rate, i.e., the dwell of the material in the mill.

The rpm of the drum depends on its diameter and ranges between 12 rpm (for rod mills of large diameter) and 40 rpm (for ball mills of small diameter). The balls and rods are 50 to 150 mm in diameter.

5. Sizing

Every stage in metallurgical treatment requires that the material be of certain particle size. The product of ore comminution varies in particle size. The latter depends on the hardness, brittleness and original shape of the ore lumps. Each size-reduction step

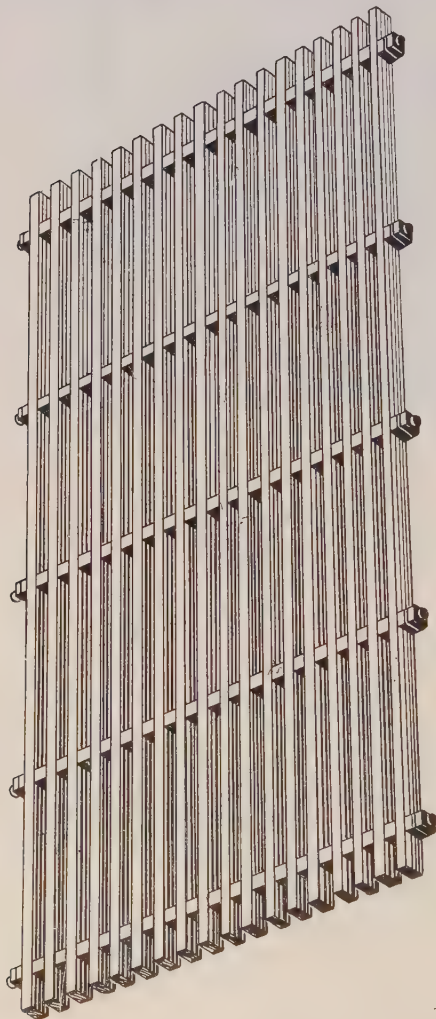


Fig. 9. Bar screen

may produce a proportion of material which is too small for the next step and will only be a burden. This is why both before and between the various stages of comminution the coarser portions of the ore

are separated from the fine fractions or graded according to size. This is accomplished by the use of a series of screens of varying mesh size, and the operation is termed screen sizing.

The simplest among screens is the bar screen (Fig. 9) which consists of parallel steel bars inclined at a pitch of 35 to 40°. The opening between the bars corresponds to the particle size desired, usually not less than 25 mm. The material slides down the pitch by gravity,

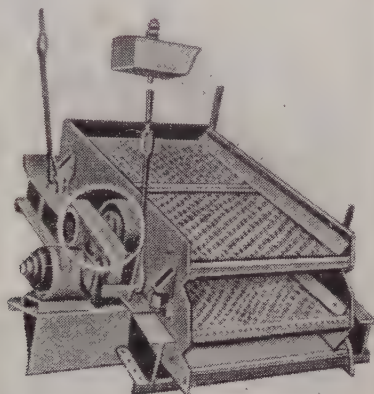


Fig. 10. Vibrating screen

and the undersize falls through the openings. Bar screens are very cheap to build, but their efficiency, i.e., the separation of fines, is very low. They are used both before and after coarse crushing.

A vibrating screen (Fig. 10) uses a metal-wire net stretched on a metal frame. The pitch of the frame is less than is necessary for the material to slide down by gravity. The frame is made to shake and vibrate by either a mechanical drive or electromagnets. The feed may be graded into several sizes by placing several nets, one above another, differing in the mesh size. Vibrating screens are used after secondary coarse and fine crushing. Their efficiency is much greater than that of bar screens.

A revolving (or cylinder) screen (Fig. 11) uses a net shaped into a cylinder. The cylinder rotates about an axis which makes a small angle with the horizontal. The material being graded slides down the pitch inside the cylinder. Several sizes may be graded in a single screen by arranging several nets of the desired mesh size concentrically.

Screen sizing is not applicable to fine sizes which tend to form larger lumps, thereby reducing screening efficiency, or produce

dust. Therefore, fines are graded in pulp form. This type of sizing is called water sizing or wet classifying. Wet classifying depends on the fact that the larger (heavier) particles settle down from the pulp quicker than the finer (lighter) ones.

A wet classifier is a vessel filled with the pulp of the material to be graded which is fed into it continuously. In the classifier, sands or quick-settling solids settle down, while the fines overflow

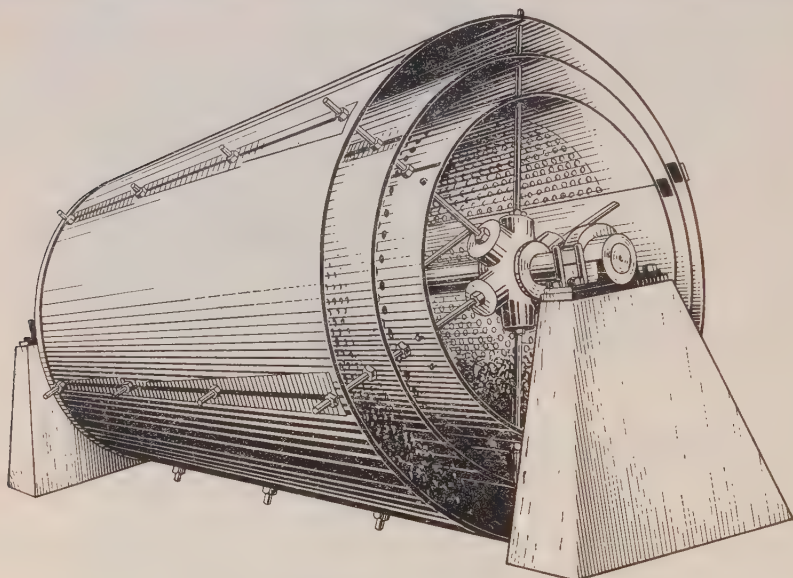


Fig. 11. Revolving (or cylinder) screen

over a baffle. The particle size in the overflow is reduced by reducing the speed of the pulp through the classifier and by making the pulp thicker.

Wet classifiers are available in a variety of designs differing in the shape of the vessel and the method of oversize discharge.

The Dorr classifier (Fig. 12) consists of a settling tank in the form of an inclined flat-bottomed trough open at the upper end. The feed enters at one end, and the liquid and slow-settling solids overflow over the baffle at the closed end. The height of the baffle can be adjusted at will. The sands are gradually moved by mechanical reciprocating rakes to the upper end where they are discharged.

The Akins classifier (Fig. 13) consists of a large-diameter spiral conveyer built into a semi-circular trough. The oversize is discharged by the spiral conveyer. This type of classifier is simpler and more reliable in service than the Dorr classifier.

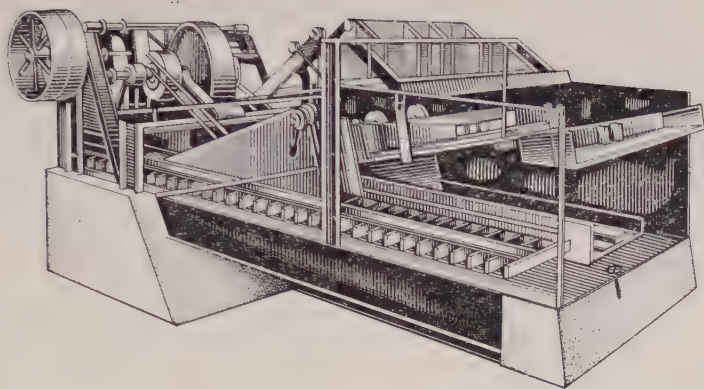


Fig. 12. Dorr classifier

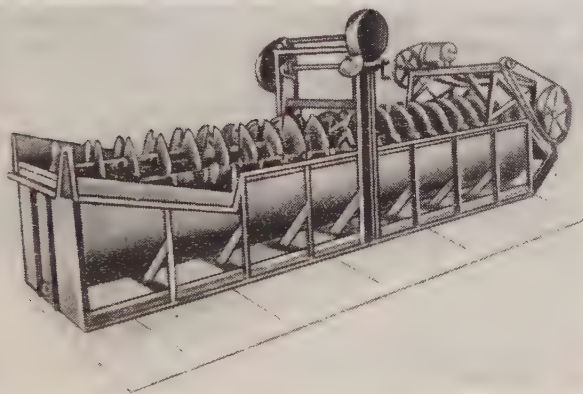


Fig. 13. Akins classifier

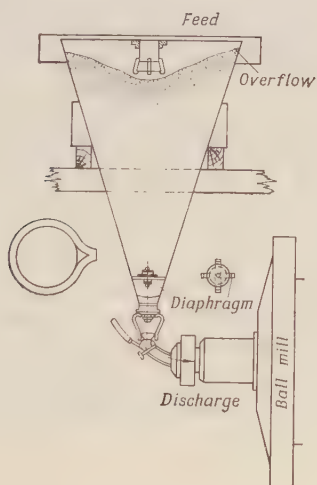


Fig. 14. Cone classifier

A cone classifier (Fig. 14) is a cone-shaped bowl with the big end up. Sands are collected at the narrow end where they are discharged by a suitable mechanism. Fines overflow the periphery and are carried off by the overflow circular launder. Cone classifiers

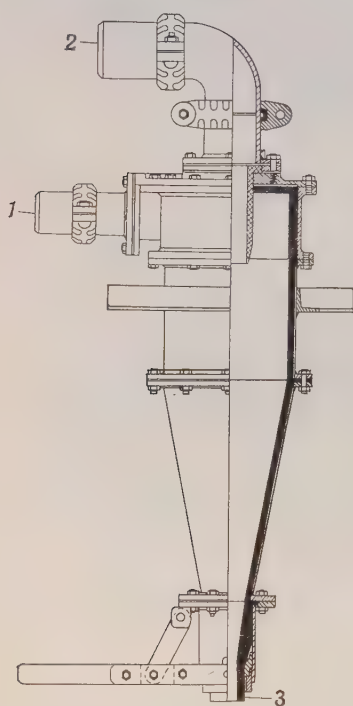


Fig. 15. Hydraulic cyclone classifier:
1—feed in; 2—overflow out; 3—sands out

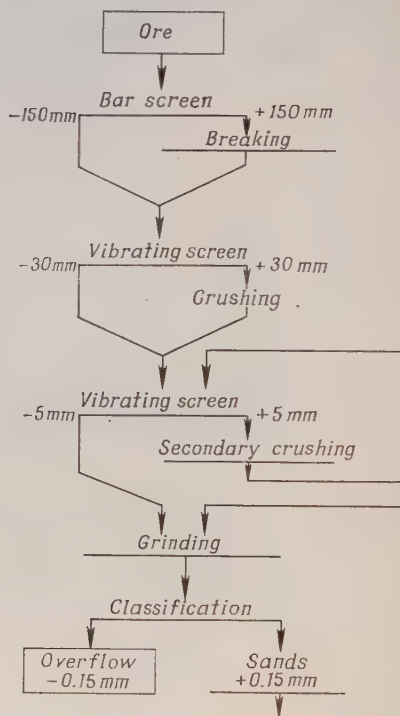


Fig. 16. Flow-sheet for ore comminution and classifying

are simple in construction as they have no moving parts. On the other hand, they are only suitable for rough sizing.

The more recent trend has been towards using hydraulic cyclone classifiers which are more compact and far more efficient than other classifiers.

The pulp is fed into a hydraulic cyclone classifier (Fig. 15) by a pump tangentially, and the stream of pulp follows a spiral path inside the classifier at a speed of 7000 to 10,000 rpm. The larger particles are brought out of the stream by centrifugal force to the walls where they slow down and settle to the bottom; the fines are carried off by the pulp through the central pipe.

The diagram in Fig. 16 gives a rough idea of how run-of-the-mine ore may be crushed, ground, sized and classified. In this case, the sands from the classifier are returned to the mill, and the overflow only carries the particles of the desired size. In such arrangement, the classifier is said to be closed-circuited with the mill. Similarly, screens may be closed-circuited with crushers.

6. Ore Dressing—Scope and Methods

Ore dressing is the processing of ores by methods which do not affect the chemical or physical characteristics of the minerals. The objective of ore dressing is to remove some of the waste product, called *tailing*, which is usually discarded. The remaining, valuable portion is called the *concentrate* and contains an increased percentage of the metal sought. Sometimes, products in between the concentrate and the tailing are obtained. They are called *middlings* and are retreated separately by suitable methods.

In some cases, complex ores may be dressed to produce several concentrates, each rich in any one metal. Such concentrates are called selective, as distinct from collective concentrates which contain several valuable metals.

Ore dressing is of vital importance to modern metallurgy. Many ores are lean to a point where their direct metallurgical treatment would be commercially unprofitable, if at all possible. Ore dressing reduces the total cost of metal extraction from ores and sometimes simplifies their further treatment. The application of ore-dressing methods has added materially to the world supply of valuable mineral products and has extended mineral reserves throughout the world for the reason that the bodies of materials not considered ores in the technical sense of the word are now classed as such. Selective separation simplifies the comprehensive utilisation of ores.

Apart from ores, ore-dressing methods are applicable to other mixtures of solids, such as by-products of metallurgical treatment, impurities and wastes.

The following methods of separating minerals are employed commercially:

(1) Hand sorting or picking in which either valuable pieces of ore are separated from worthless pieces or vice versa on the basis of differences in their colour, lustre and lump shape. It may be accomplished right at the face or on an ore-sorting conveyer.

(2) Separation on the basis of differences in the hardness, brittleness and lump shape of minerals due to which some minerals are crushed more readily than others, so that subsequent screening can efficiently liberate the valuable fraction from tailings.

(3) Separation based on friction, in which the difference in the rate of movement down an inclined surface is utilised.

(4) Electrostatic separation based on differences in the electrical conductivity, capacitance and dielectric properties of minerals.

(5) Magnetic separation methods which separate minerals owing to difference in their magnetic properties.

(6) Gravity separation which utilises differences in the specific gravity and settling velocity of minerals in liquids or air.

(7) Heavy-media (or float-and-sink) separation, a gravity method which depends on the use of a suspending medium of controlled specific gravity in which some minerals sink while others float. Suspending media are various organic liquids, solutions or suspensions.

(8) Flotation which is based on the selective attachment of air bubbles to the desired solid particles in aqueous suspensions after treatment with suitable reagents.

Of the eight methods described above, widest commercial use has to date been made of flotation, gravity separation, and magnetic separation, in the order given.

7. Flotation

Flotation boils down to the following. Small amounts of flotation reagents are added to the suspension of solids (pulp). The pulp is then made to flow continuously through a series of cells where the pulp is vigorously agitated and air is blown into it under pressure. The air is broken into tiny bubbles which are distributed throughout the volume of the pulp, attaching themselves to those solid particles which have become water-repellent after reagent treatment. The bubble-particle aggregates float to the surface of the suspension where a mineral-laden froth forms.

The reagents that form water-repelling films on the surface of some minerals are called collectors. They are high-molecular-weight organic compounds. The most common among them are xanthates, carboxylic acids and their salts. Collectors will attach themselves only to minerals with a definite chemical composition and lattice structure. No air bubbles can attach themselves to mineral particles which have not absorbed any of the flotation reagent. Therefore, they remain in the pulp.

Flotation also uses other reagents, known as frothers, which increase froth stability within desired limits. For their action, frother depend on their ability to reduce the surface tension of water. Frothers are various organic compounds, such as oils, soaps, and resins.

Flotation uses very small quantities of collectors and frothers—usually not more than 50 to 300 grams per ton of ore. This is because they are surface-active compounds, or surfactants, and concentrate

at the interface between the water and solid particles and air bubbles in relatively large amounts.

Minerals similar in chemical composition, such as sulphides of copper, lead and zinc, exhibit an almost equal ability to absorb collectors; for this reason, when present in the same suspension, they will tend to froth together. For the purpose of selective flotation, this tendency may be controlled by supplementary reagents, known as depressors. Depressors are inorganic compounds which form films on solid particles, thereby preventing the absorption of collectors. The film is produced through a chemical reaction between the depressor and the surface layer of the mineral.

The collector effect, on the other hand, may be enhanced by other supplementary reagents, called activators. They are inorganic compounds soluble in water. Added to the suspension, an activator can destroy or modify the depressor film on the solid particles so that they are now able to absorb the collector ions or molecules and become floatable.

A suitable example of selective flotation is provided by the dressing of a lead-zinc ore containing lead glance (PbS), zinc blende (ZnS), pyrite (FeS_2) and quartz (SiO_2). The ore may be floated to obtain a collective lead-zinc concentrate. This will only require a collector, a frother and a medium of such pH at which the pyrite will not be floated. Then the lead and zinc minerals will go into the froth, and the pyrite and quartz will remain in the pulp. In the case of selective flotation, the zinc blende will be depressed by adding sodium cyanide and zinc vitriol to the feed. These depressors form a film of insoluble zinc cyanide on the surface of zinc blende particles, but do not react with the lead glance. Then the collector and frother are added, and the PbS is floated alone. After the lead-laden froth is collected, the ZnS is activated by adding some copper sulphate. The surface of the zinc blende particles is covered by a new film of copper sulphide which readily reacts with the collector. Now the zinc blende goes into the froth, and the zinc-laden froth is skimmed. In still another refootation, the pyrite concentrate is obtained. The remaining tailings go to waste.

In some cases, no depressor is used during the first flotation, and a collective lead-zinc concentrate is obtained, which is then refoated in the presence of some depressor, the lead glance caused to go into the froth, and the zinc concentrate left in the pulp.

Flotation is widely employed for dressing a large variety of ores. As often as not, its medium is made acidic or basic by adding, in the latter case, some lime to the pulp.

Commercial flotation machines operate continuously: the pulp is fed into a machine uninterruptedly, and the froth product and the tailings are discharged likewise continuously.

In flotation machines the pulp can be aerated either pneumatically or mechanically. Mechanical flotation machines are the most commonly used.

In a typical mechanical flotation machine the tank is of rectangular cross section, divided by transverse partitions into cells (Fig. 17). The pulp is fed through a box 1 down a pipe 2 and into the first cell

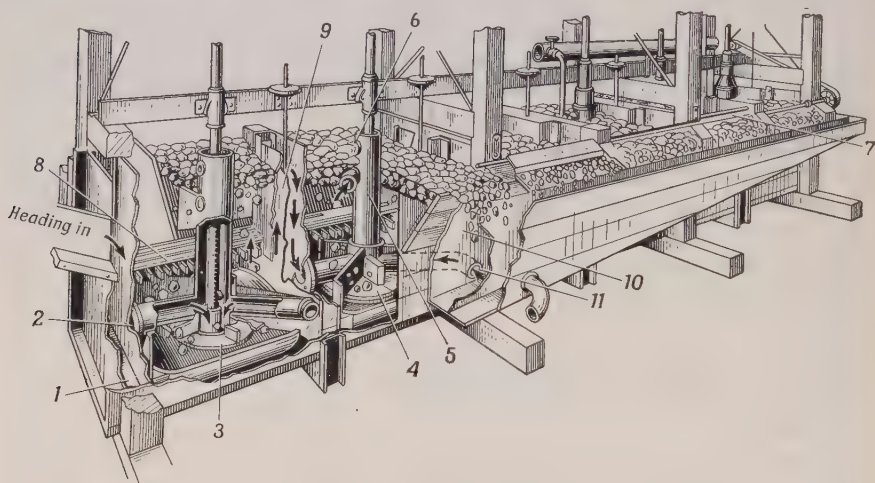


Fig. 17. Mechanical flotation machine

of the machine. In the cell, the pulp is vigorously agitated by a high-speed stirrer 3 covered by a disk 4 from above. The stirrer is a wheel with vanes of hard steel. It rotates at 275 to 600 rpm and sucks in air from a pipe 5 through a hole 6. The pulp mixed with finely divided air bubbles rises to a settling zone which lies above a grill 8. From the first cell the pulp flows over a baffle 9 into an intermediate box, and so on, until it has gone through all the cells. The tailings are discharged continuously from the last cell. The froth is driven by paddles 7 into a launder. In the case of reflation, the froth is directed into another launder 10 whence it is recirculated to the cells over pipes 11.

The flow-sheets of flotation may be fairly complicated even when only one mineral is to be separated from the ore. They become still more complicated when two or three different concentrates are to be obtained from the same ore. Figs. 18 and 19 show simplified flow-sheets of simple (or bulk) and selective (or differential) flotation.

The principal criteria of flotation efficiency are the recovery of the metal into the concentrate and its content in the concentrate

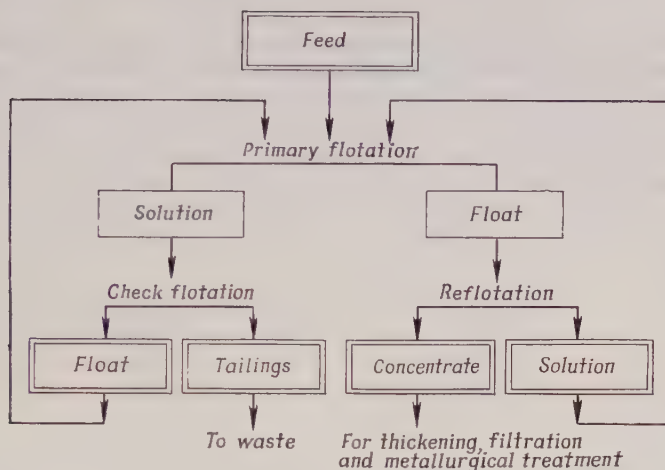


Fig. 18. Flow-sheet for simple (or bulk) flotation

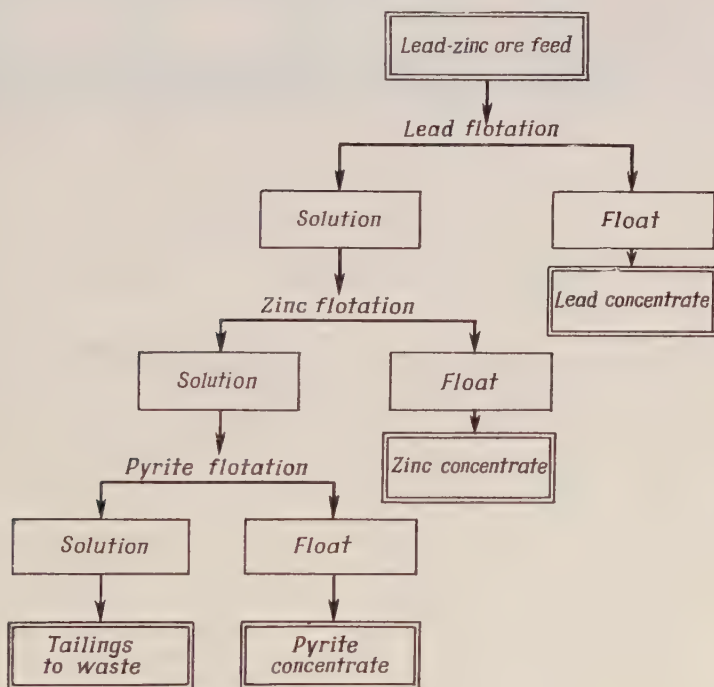


Fig. 19. Flow-sheet for the selective (or differential) flotation of lead-zinc ore

(in per cent). The recovery varies within broad limits (70 to 98 per cent) and is governed by many factors. Sometimes, as much as 85 to 94 per cent of the metal can be removed into the froth.

For successful flotation, the ore should be finely divided so as to break up mineral aggregations. Because of this, the cost of grinding often exceeds that of flotation proper and other associated operations. An approximate break-down of the overall cost of ore concentration by flotation (in per cent) is as follows:

Crushing	5.9-18.8
Grinding	26.3-75.3
Flotation	25.1-46.8
Dewatering and drying	10.5-19.4
Other operations	3.2-10.5

These figures add forcefulness to the principle "Never Crush or Grind Too Much". It may be added that too fine a material has often an adverse effect on flotation, since over-ground minerals show a reduced difference in flotation properties than particles of an optimal size.

At present, flotation is often carried out with the material being ground in stages. The first to be flotated are relatively large ore particles. The concentrate thus obtained is then further comminuted prior to a next stage of flotation. This practice reduces the cost of comminution and improves the quality of the concentrates.

8. Gravity Concentration

Two of gravity concentration processes are jigging, the removal of the lighter portions of an ore by means of a stream of water or air which rises through a bed of coarse ore particles, and tabling, a similar removal by passing a mixture of ore and water over an inclined vibrating table.

Two forces act upon a particle falling down in a viscous medium. These are gravity and friction. At first, the particle moves with some acceleration. As its velocity increases, the friction against the medium also increases. Therefore, the particle attains with time some constant velocity, called critical velocity.

In jigging, the particles falling out of the feed are deposited on the bottom in layers according to their specific gravity. This separation is better when all the particles in the feed are of the same size, which condition can be attained by preliminary screening or classifying. The latter may, however, be dispensed with, when the particles fall from a low height and their velocity, very far from critical, is mainly dependent on their specific gravity. Jigging is usually conducted in a pulsating stream of water which may move either up and

down or only up. This feature limits the height of fall and prevents particles from being caught by other particles.

A jig is a water-filled tank with a metal screen installed below the water level. The pulsating effect is produced either by the water (plunger and pulsator jigs) or by the swinging screen (or pan).

A plunger jig (Fig. 20) has wooden cells each of which is divided into a plunger and a jiggling compartment by a partition 3 which

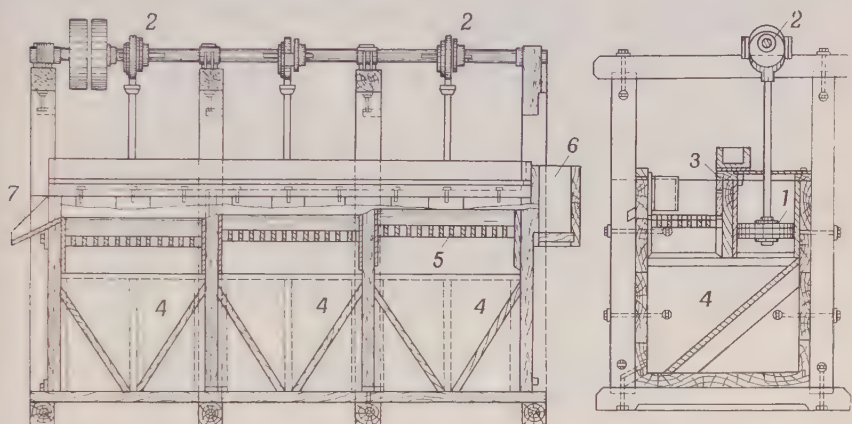


Fig. 20. Plunger jig:

1—plunger; 2—eccentric; 3—partition; 4—cell; 5—screen; 6—charging box; 7—launder

does not reach the bottom by a short distance. The plunger compartment houses a plunger 1 actuated by an eccentric 2, and the other compartment is occupied by a stationary screen. The screen in every next cell is placed 100 mm lower than that of the preceding cell.

Each screen carries a bed of finely divided magnetite or small metal balls. The specific gravity of the bed should be anywhere between those of the minerals to be separated. Large sizes (8 to 10 mm) may be jigged without any bed.

The feed is fed into the first cell, passes consecutively through all of them, and is discharged into a launder 7. The pulsating stream of water in the screen meshes and the pores of the bed is produced by the plungers completing 100 to 300 strokes per minute with an amplitude of 0.5 to 8 cm. The quick-settling heavy grains of the minerals pass through the pores in the bed and are collected on the bottom of the cells 4 whence they are recovered at regular intervals. The slow-settling lighter grains are carried on by the horizontal flow of feed. The capacity of this machine is 10 to 40 tons of ore per square metre of the screen per day.

A pulsator jig is shown in Fig. 21, with the pulsator, which is the key component of the jig, at right. Water is admitted into the pulsator by a pipe 3 where it is directed under a rubber diaphragm 4. Overcoming the spring 5, the water opens the valve plate 6 and enters the jig. As the pressure drops instantaneously, the valve plate

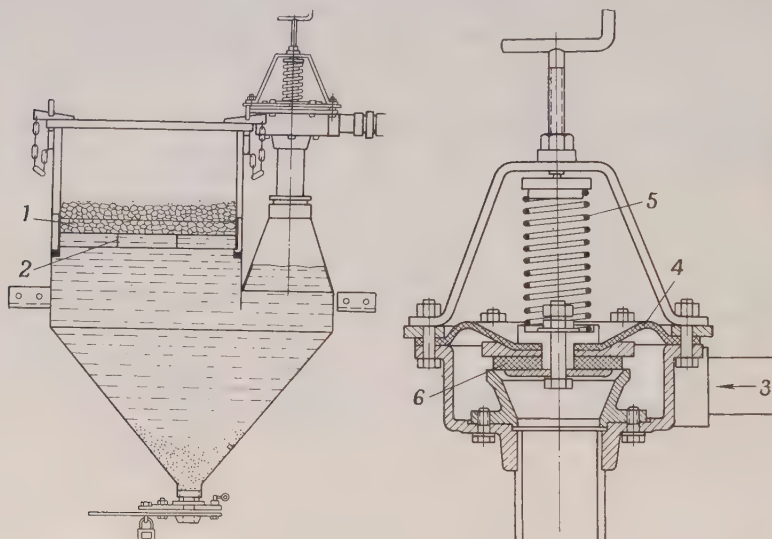


Fig. 21. Pulsator jig:

1—bed; 2—screen; 3—water-supply pipe; 4—diaphragm; 5—spring; 6—valve plate

closes. In this way a directional and pulsating stream of water is produced in which jigging takes place. The rate is 600 pulsations per minute.

Among the advantages offered by pulsator jigs are high recovery, low power consumption, and the absence of any mechanical drive.

High-rate pulsator jigs operate at 1500-2000 pulsations per minute. In exceptional cases, the rate of pulsations may reach 3000 to 4000 per minute. Combined high-rate plunger and pan jigs give good results in jigging the fine (sludge) fractions of ores.

Tabling involves the use of concentrating tables (Fig. 22). The deck of a concentrating table is usually covered with linoleum, canvas, rubber or cement. Besides, the deck has wooden riffle cleats. The deck is set up on the bedframe so that it makes an angle of 9° with the horizontal.

The heading which should contain particles of about the same size is fed into a charging box whence it flows in a flat stream onto the deck. A suitable drive causes the deck to move to and fro in a

longitudinal direction in jerks recurring at a rate of 230 to 300 per minute and with an amplitude of 12 to 30 mm. The stream of water tends to carry every particle at right angles to the axis of the deck, while the jerks send it along the deck. As a result, the particles move in a path which makes an angle with the deck diagonal. The

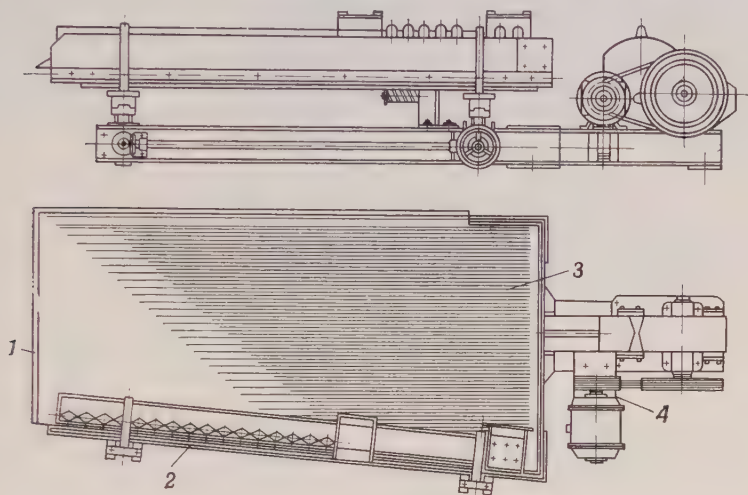


Fig. 22. Concentrating table:

1—deck; 2—charging box; 3—riffles; 4—shaker

heavier a particle, the greater is its travel along the deck with each jerk. For this reason, the material being jigged fans out on the deck so that the minerals with different specific gravities come off the deck at different points.

9. Magnetic Separation

By their attraction to a magnet, minerals may be classed into strongly magnetic, medium magnetic, weakly magnetic, and non-magnetic. Taking the attraction of iron for 100, for strongly magnetic materials this figure will be anywhere between 3.21 and 40.18 (magnetite, Fe_3O_4), for medium magnetic between 0.40 and 1.82 (limonite, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, wolframite, $(\text{Fe}, \text{Mn})\text{WO}_4$, etc.), and for weakly magnetic, to which most of the minerals of non-ferrous metals belong, the figure will be less than 0.37.

Magnetic separation may also be applied to metal-working wastes, for many non-ferrous metals and alloys are non-magnetic. Mixtures of non-ferrous metals and iron (turnings, drillings, scrap) can conveniently be separated by magnetic methods.

Magnetic separation is carried out in magnetic separators. The material to be treated may be fed suspended in water (wet magnetic separation) or in air (dry magnetic separation). Large-size materials (120 to 150 mm across) are usually treated by dry magnetic separation. Small-size materials (less than 6 or 8 mm across) may be treated by both dry and wet methods. In the case of small-size materials, wet separation gives better results, as water prevents magnetic and non-magnetic particles from sticking together.

Finely divided ores and concentrates of non-ferrous metals are treated in magnetic separators widely varying in design. One of them is a disk magnetic separator (Fig. 23).

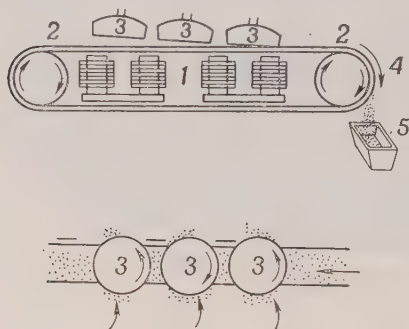


Fig. 23. Diagram of a disk magnetic separator:

1—electromagnets; 2—endless belt;
3—disks; 4—drive pulley; 5—re-
ceiver for non-magnetic material

The disk magnetic separator for the dry separation of weakly magnetic ores has an endless belt 2 passed over pulleys 4 one of which is driving. Placed between the carrying and return runs of the belt are adjustable electromagnets. Over the carrying run of the belt are placed rotating iron disks 3 each of which resembles an inverted bowl with sharp edges. The disks rotate so that their right-hand sides are nearer to the belt than the left-hand sides. Through induction, a magnetic field concentrates at the sharp edges of the disks, so that it is stronger on the right than on the left. The feed is allowed to pass beneath the disks, and the magnetic minerals are attracted by the edges of the disks. The diameter of the disks is greater than the width of the pole pieces and belt. Therefore, in rotating, the disk edges are recurrently demagnetised and shed off the attracted pieces into a receiver 5. With three disks rotating in magnetic fields of different strength and at different angles to the belt, it is possible to separate six products differing in magnetic susceptibility. The separator in question efficiently separates minerals of tungsten, iron and tin.

Drum separators are intended for coarser materials. They may be used to liberate strongly magnetic ores from the gangue or to

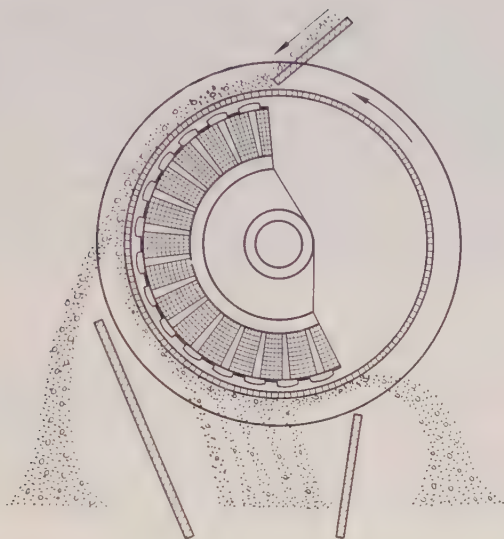


Fig. 24. Drum-type magnetic separator

pick out "tramp" iron (tools, iron scrap) which may cause breakage to crushers, if the ore is to be crushed.

A drum separator (Fig. 24) consists of a rotating brass cylinder inside of which a stationary electromagnet is placed. The operation of the separator is self-evident from the figure. It may serve as the end pulley of an ore belt.

10. Dewatering

Ore concentrates are most often produced as water suspensions. Before they can be processed any further, especially by pyrometallurgical methods, concentrates have to be completely dewatered. Sometimes, it is essential to dewater the shipped product in order to reduce shipping costs. Besides, poorly dewatered materials will freeze at sub-zero temperatures so as to be difficult to handle.

Dewatering is resorted to not only after ore dressing, but also in the case of hydrometallurgical treatment. In the latter case, the operation is more difficult, as the ore or valuable residue has to be washed to remove the entrapped reagent.

Dewatering can be accomplished by three methods: thickening, filtering, and drying. Thickening is the cheapest of all, but it can reduce the water content of the pulp only to 40 or 50 per cent. Filtering is more expensive, but leaves only 10 per cent moisture in the

residue. Drying is the most expensive of all, as it involves the burning of fuel, but dewatering in this case is practically complete.

In the case of thickening, the pulp is allowed to settle in thickeners (Fig. 25). The clear liquid is called the overflow, and the residue is called the underflow.

The larger particles settle from the pulp quicker than the smaller ones. To speed up their settlement, use sometimes is made of flocculators and coagulators, such as lime, glue, etc. As a result, the smaller particles stick together to produce larger pieces.

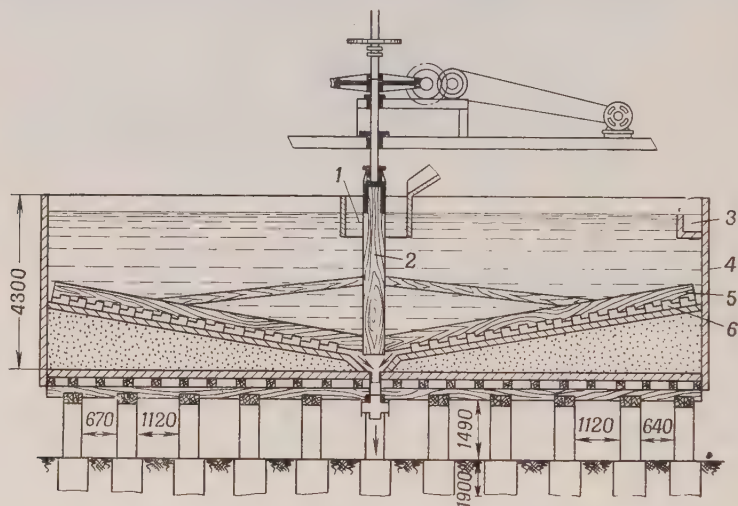


Fig. 25. Suspension-shaft thickener:

1—central well; 2—shaft; 3—launder; 4—tank; 5—spider; 6—rakes

A thickener is a cylindrical tank of wood or reinforced concrete up to 100 m in diameter. The slurry feed is admitted into the tank by a central well. The tank is filled to the level of the circular overflow launder running at its periphery. The solid particles settle on the conical bottom slightly inclined towards the centre where a centre discharge cone is located. The discharge cone is fitted with gate valves and calibrated attachments. From the thickener the solution is conveyed by pipes into an intermediate tank from which it is pumped where desired. The settled solids are swept to the central discharge by inclined rakes mounted on a spider which is in turn carried by a shaft. As the rakes complete one revolution during two to eight minutes, they cannot interfere with settling.

In large thickeners with a diameter of more than 15 or 18 m, the central shaft is replaced by a stationary column, and the spider

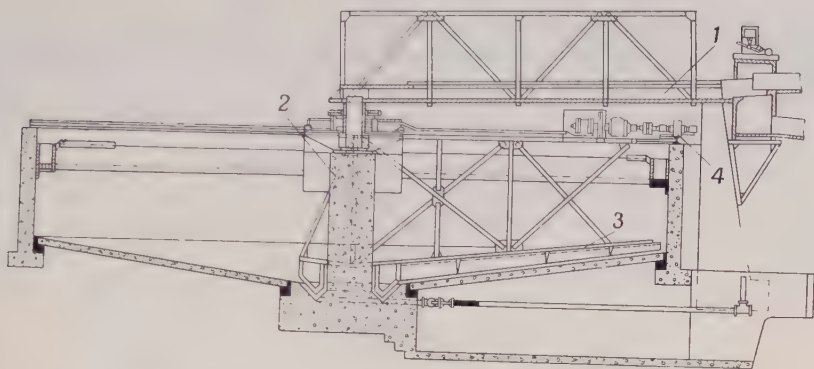


Fig. 26. Rim-driven thickener:

1—feed launder; 2—column; 3—centrepiece; 4—carriage

by a centrepiece. The centrepiece is made to rotate about the column by a carriage which rides the rim of the tank (Fig. 26).

The capacity of thickeners is expressed in the surface area of the bottom required to obtain 1 ton of solids in the thick underflow product during twenty-four hours (sq m per ton-day). The

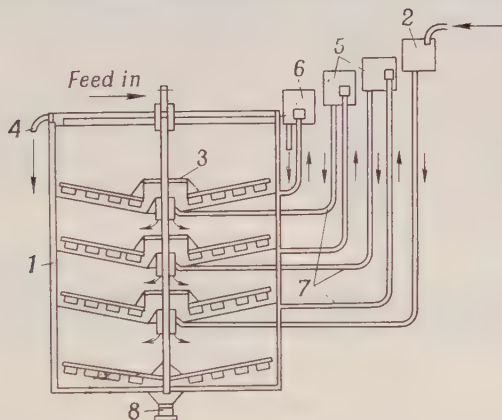


Fig. 27. Multitray thickener:

1—tank; 2—wash-water tank; 3—trap; 4—overflow pipe; 5 and 6—recycling tanks; 7—piping; 8—underflow discharge

capacity may vary within broad limits, depending on the properties of the slurry feed. In thickening a flotation concentrate from 10 to 40 or 60 per cent of solids, the capacity is 1.2 to 1.7 sq m/ton-day.

A multitray thickener (Fig. 27) is in fact several superimposed thickening compartments in a single tank. Multitray thickeners

are especially efficient in treating decantation slimes. They are more attractive where an increase in the height of a building is cheaper than an increase in its surface area.

Thickening may also be accomplished by the hydraulic cyclones described earlier.

Filtration of the pulp is based on screening the liquid through a porous material which is impervious to solid particles. The filter medium may be cotton or woollen fabrics, as well as fabrics from glass and synthetic fibre. It is essential that the filter medium be chemically stable with respect to the solution being filtered. The

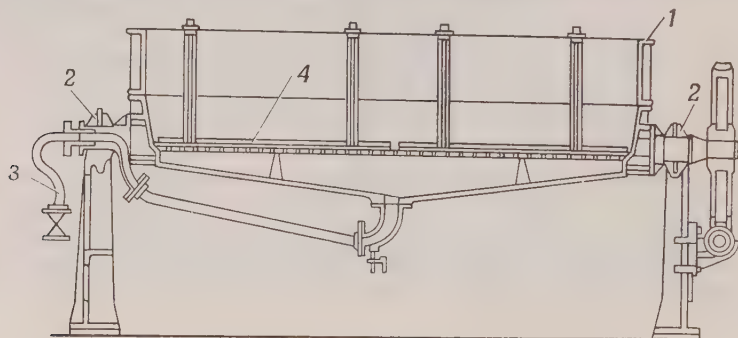


Fig. 28. Nutsch filter:

1—tank; 2—trunnions; 3—vacuum-line; 4—false bottom

rate of filtrate flow and, consequently, the capacity of filters depend on pressure difference and head loss in the pores of the cake and the filter medium. As the cake grows thicker, the rate of filtrate flow slows down. The bridging of the pores in the filter medium by solid particles also acts in the same direction.

Commercial filters are classed into vacuum filters in which the pressure differential is built up by the vacuum in the filtrate collector, and filter-presses in which the pressure is applied over the filter medium and surrounding slurry or feed. This chapter only deals with vacuum filters, while filter-presses are described in Sec. 85.

Fig. 28 shows an intermittent vacuum filter, also known as the Nutsch filter. Its construction is self-evident from the diagram.

A drum-type continuous rotary vacuum filter (Fig. 29) consists of a hollow perforated cylinder covered with a filter medium and rotatable in trunnions. The filter medium is held in place by a wire spiral. The drum is divided longitudinally into a number of shallow compartments. Each is connected individually to a multiple valve hub, which is faced with a wear plate and turns against a stationary valve cap. The cap is equipped with bridges to separate vacuum and flow-back recesses.

In operation, as the drum rotates, each compartment in turn is subjected to cake-building vacuum during submergence, washing and drying vacuum upon emergence, and blow-back take-off at discharge. The whole operation is continuous and automatic. The

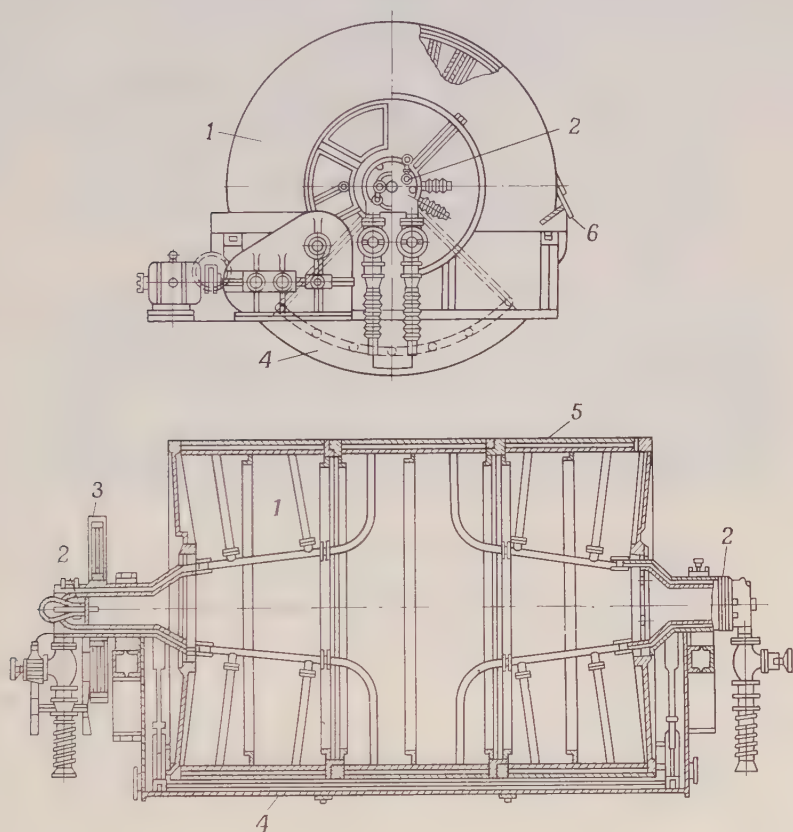


Fig. 29. Drum-type continuous rotary vacuum filter:

1—drum; 2—multiple valve hub; 3—drive; 4—tank; 5—perforated sheet and filter medium; 6—cake scalper

drum rotates at 0.13 to 2 revolutions per minute, and the cake on its surface is 6 to 15 mm thick. Filter capacity is rated in the weight of dry solids per hour per square unit of area of the filter medium. For flotation concentrates, the capacity is anywhere between 0.15 and 0.5 ton/hr/sq m and depends mainly on the particle size and the liquid-to-solid ratio of the feed. The residual moisture content of the cake depends on the same factors.

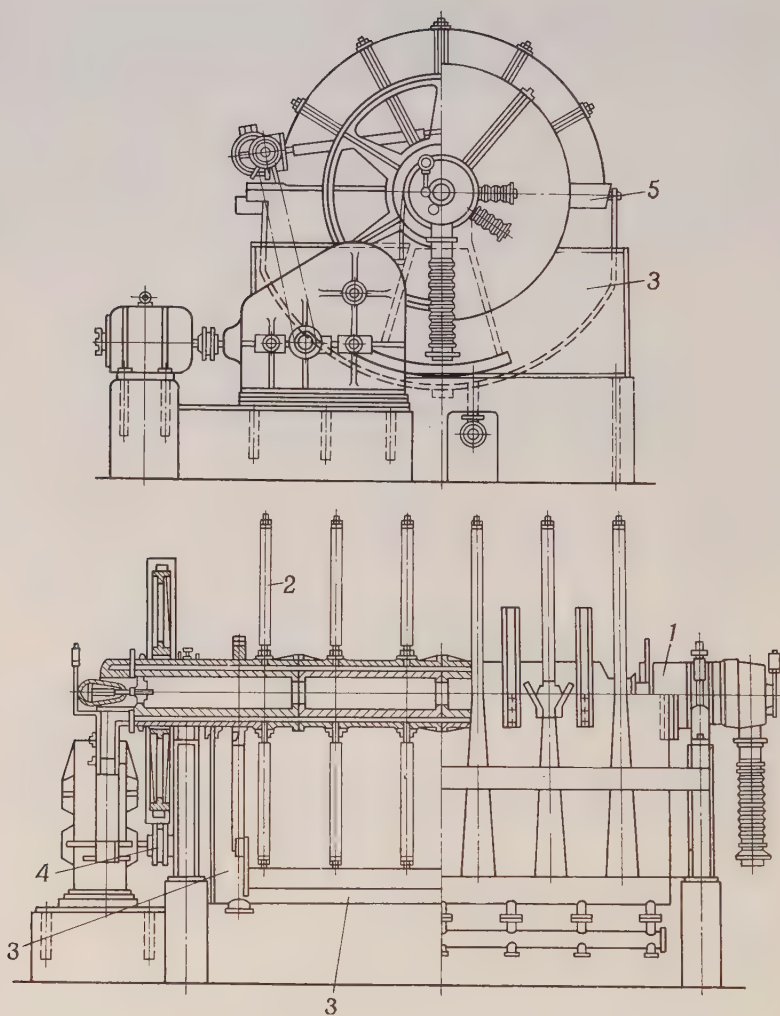


Fig. 30. Rotary disk vacuum filter:
 1—shaft; 2—disks; 3—tank; 4—drive; 5—cake scalper

Rotary disk filters are similar to drum filters in general operation (Fig. 30), but have sectorised filtering disks with filter medium on each side. A number of disks mounted vertically on a common horizontal shaft, which acts as a drainage line, are suspended in a filter tank. The grooves in the sectorised disks, which may be of wood or metal, terminate at the central shaft. The cake is removed into

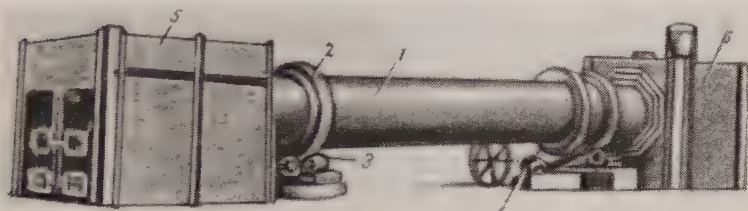
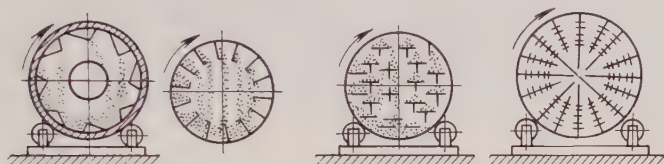


Fig. 31. Rotary kiln drier and baffles:

1—drum; 2—rim; 3—rollers; 4—drive; 5—firebox; 6—charging end

inclined troughs separately from each disk. Given the same overall dimensions, disk filters have a greater filtering area and greater capacity than drum filters.

Dewatering by drying is based on the evaporation of water. The rate of evaporation is proportional to the difference in the vapour pressure above the material being dried and in the surrounding gaseous medium. The water vapour pressure above the material rises with drying temperature. In the surrounding medium, the vapour pressure is decreased as the velocity of the medium is increased. It should be noted, however, that the increase in gas velocity can speed up drying to a certain limit only, as the removal of vapours from the surface of the material into the gas is limited by diffusion. Furthermore, the stream of gas moving at a high velocity will turn too much material into dust. The bed of the material being dried should be as thin as possible and well stirred.

Driers are available in a great variety of designs. The most common among them is a rotary kiln drier (Fig. 31). Its key part is a plate-steel drum 8 to 12 m long and 1.5 to 2 m in diameter. The drum makes

an angle of 1 or 2 degrees with the horizontal. Its two smooth rims are carried by rollers whose races are set up on a foundation. A toothed rim engages the drive gear of a reduction train which is actuated by an electric motor. The drum rotates at 3 to 8 revolutions per minute. Inside the drier body there are radial or other baffles which stir the material as it rides up the sides and falls back. The feed is continuously charged into the raised end of the drier body by a mechanical feeder, and travels towards the opposite end as the drier rotates. The hot gases produced by burning some fuel travel in a counter-flow. Such an arrangement makes it possible to remove traces of moisture efficiently by the hottest and driest gases.

Part Two

THE METALLURGY

OF IRON

Chapter III

IRON AND ITS COMMERCIAL ALLOYS

11. General

Pure iron in the solid state is a silver-white, tough and malleable metal. Its density at 20 C is 7.87 ± 0.001 g cu cm. Its melting point is 1539 ± 1 C and its boiling point 2450°C. In melting, iron expands by 4.4 per cent. The latent heat of fusion is 65 cal/g. The thermal conductivity of iron is one-sixth to one-seventh of that of silver and is half as great as that of aluminium. Its electrical conductivity is one-fifth to one-sixth of that of silver and is one-third of that of aluminium.

In 1868, Chernov of Russia discovered that iron was capable of undergoing crystal transformations on heating from room temperature to melting point, and determined the points at which those transformations occur (critical points, Fig. 32). According to Chernov, the conditions of heat treatment and subsequent cooling have a decisive effect on the structure and properties of iron alloys. Solid iron exists in two crystal modifications: body-centred cubic (alpha, beta and delta iron) and face-centred cubic (gamma iron). At 768°C (the Curie point) alpha iron, which is ferromagnetic, becomes paramagnetic without a change in crystal structure. At 910°C alpha iron

transforms to gamma iron. At 1390°C gamma iron transforms to delta iron, and at 1539°C the metal melts.

In chemical compounds iron may be divalent and trivalent.

Iron dissolves in acids, is oxidised by halogens and oxygen. In reacting with oxygen, iron forms ferrous oxide FeO , ferrous-ferric

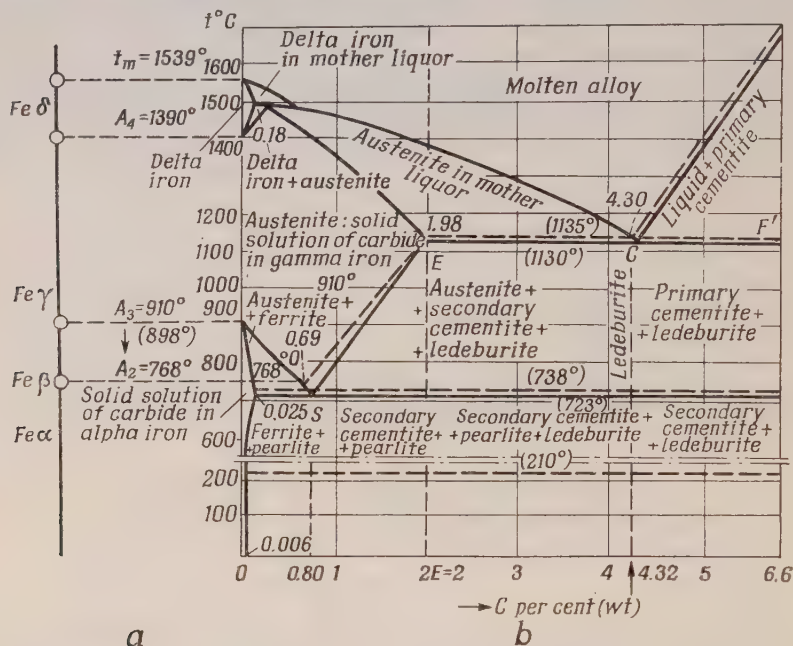


Fig. 32. Iron-carbon system:
(a) critical points of iron; (b) constitution diagram

oxide $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ or magnetite Fe_3O_4 , and ferrous oxide or hematite Fe_2O_3 . The latter two oxides make up the most important minerals of iron.

Ferrous oxide FeO occurs in siderite ($\text{FeO} \cdot \text{CO}_2$), ilmenite ($\text{FeO} \cdot \text{TiO}_2$), fayalite ($2\text{FeO} \cdot \text{SiO}_2$), magnetite and some other minerals.

Among the compounds iron makes with sulphur, the most common are pyrrhotite (Fe_7S_8) and pyrite (FeS_2), as well as minerals of copper and iron. At low temperatures iron reacts with carbon monoxide to form carbonyl, $\text{Fe}(\text{CO})_5$. With carbon, iron forms carbide (cementite), Fe_3C .

Chernov's discovery of critical points has formed the basis of the iron-carbon constitution diagram (Fig. 32b) which relates the

phase and structural transformations in iron-carbon alloys to temperature.

An alloy containing 6.66 per cent C has the composition of iron carbide, Fe_3C . The point *E* in the diagram shows the maximum solubility of carbon in solid iron. Steels are alloys of iron and carbon, containing up to 2 per cent carbon. Alloys carrying more carbon (usually over 2.5 per cent) are called pig irons.

The carbon content determines many of the properties of a steel. As it increases, the steel becomes harder and stronger, but its ductility is reduced. Apart from carbon, the properties of a steel may be affected by other elements, such as manganese, silicon and chromium.

Any steel contains from 0.2 to 1 per cent manganese which may run more than that in high-manganese (alloy) steels. Manganese increases the hardenability of steel, raises its hardness, ultimate strength, yield point, but reduces its ductility (per cent elongation, reduction of area, and impact strength).

The most common grades of steel contain not over 0.4 per cent silicon, while special types of steel may have over 0.5 per cent silicon. Silicon raises the hardenability and ultimate strength of steels.

Nickel, chromium, tungsten, molybdenum, vanadium, cobalt, titanium and some other elements are alloying additions introduced into a steel in order to impart it some special properties. A steel containing some of these additions is called an alloy steel.

Sulphur, phosphorus and dissolved gases are harmful impurities in steels. Sulphur makes a steel red-short, a heterogeneity of structure across an ingot, and impairs its mechanical properties. For this reason, the sulphur content in a steel must be kept to not over 0.02-0.05 per cent.

Phosphorus makes a steel cold-short and reduces its impact resistance. The maximum phosphorus content in steels must not exceed 0.02-0.03 per cent.

All steels may be divided into three broad classes:

- structural steels (for boilers, ball-bearings, springs, and other machine elements);
- tool steels which go to make tools;
- special steels (stainless, acid-resistant, heat-resistant, magnetic, etc.).

Iron is the fourth most abundant element. Its abundance ratio is 4.2 per cent. This fact, together with the accessibility of its deposits and the comparatively low cost of extraction, as well as its diverse and high engineering properties have all made iron and its alloys the most used materials.

Chapter IV

THE METALLURGY OF PIG IRON

12. Iron Ores

The ores of iron are classed according to the iron mineral which is predominant. They are, in the order of theoretical percentage of iron content in the mineral:

Magnetites (black ores), Fe_3O_4 , 40 to 70 per cent iron. They are very hard and strongly magnetic.

Magnetites also occur in a mixture with silica (35-37 per cent iron and up to 60 per cent silica) and are then known as ferruginous quartzites. Ferruginous quartzites call for special methods of dressing and preparation prior to smelting.

Hematites (red ores), Fe_2O_3 , 45 to 65 per cent iron. Hematite is easily reduceable to metallic form, and iron from it can be produced at a lower cost. Hematite usually contains little phosphorus and sulphur.

Limonites (brown ores), $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, with a varying amount of water of combination. Limonites contain 57.14 per cent iron and 25.3 per cent water. Usually, hydrated hematites contain 25 to 50 per cent iron. Limonites are porous minerals.

In some deposits, hydrated hematite occurs in dense lumps; in other deposits it is finely divided. The gangue is argillaceous, sometimes siliceous-aluminiferous. In most deposits, the ore carries much phosphorus, sulphur and sometimes arsenic. Their preparation for iron extraction should include wet dressing which easily liberates the iron mineral from the argillaceous gangue.

Manganese ores constitute the basic source of manganese iron and alloys. The predominant minerals are pyrolusite (MnO_2), braunite (Mn_2O_3), manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and hausmannite (Mn_3O_4).

Manganese ores contain 20 to 52 per cent Mn. Where high-manganese alloys are to be produced, the presence of iron oxides is undesirable, as they are fully reduced to metallic form, thereby lowering manganese content in alloys.

Phosphorus runs not more than 0.15-0.2 per cent in manganese ores. Where pyrolusite is the predominant mineral, the ore is powdery. If braunite is the predominant mineral, the ore is lumpy. The siliceous-aluminiferous gangue can be easily removed by wet dressing.

Table 3 summarises the characteristics of the ores discussed above.

Table 3

Approximate Composition of Iron Ores
(per cent)

Ore	Fe ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	CaO	MnO	P	S	Loss on ignition	H ₂ O hydration	Fe	Mn
Magnetite												
A	74.1	16.7	2.6	2.4	0.4	Traces	—	Traces	—	—	65.2	2.0
B	79.5	—	6.8	2.2	4.7	0.9	0.02	3.2	—	—	56.7	0.1
C	43.8	15.1	20.3	6.3	11.5	1.0	—	0.01	—	—	42.4	0.3
Hematite												
A	94.6	—	2.7	2.2	0.2	—	0.01	—	1.6	—	66.2	—
B	86.6	—	9.9	1.9	—	—	0.05	—	2.2	—	60.5	—
C	71.4	—	10.8	8.6	1.2	0.7	0.60	—	—	—	50.0	—
Quartzite												
A	70.9	—	25.3	0.6	0.4	0.3	0.08	—	3.5	—	49.6	—
B	57.3	—	35.0	2.4	1.5	2.0	0.16	—	3.8	—	40.1	—
Brown ore												
A	76.3	—	3.4	2.5	1.7	1.8	0.01	0.01	—	12.0	53.4	1.0
B	72.0	—	13.6	3.0	0.4	0.1	0.08	0.02	9.5	—	50.4	1.1
C	58.6	1.1	16.7	5.5	1.5	1.0	1.17	0.27	11.6	9.4	41.8	0.6

13. Preliminary Treatments of Iron Ores

Of late, the treatment of ores preliminary to smelting has acquired special importance. One reason for this trend has been the ever increasing use of leaner ores. Another reason has been the desire to improve smelting economy.

This preliminary treatment includes crushing, screening (in order to separate fines), sizing, averaging, concentration (all of these operations have been described already), and agglomeration either by briquetting with binders, or sintering by partial fusion.

Sintering. An ungraded ore would severely handicap the operation of the blast furnace. The fines would clog the space between the lumps, thereby preventing the free flow of the gases. A large proportion of fines is usually carried off as flue dust. Besides, fines account on the average for 40 per cent of the ore mined in the Soviet Union. All this calls for the use of agglomeration, mainly by sintering.

Prior to sintering, the fine ore and flue dust are thoroughly mixed with 4 to 6 per cent fuel (coke breeze) and 25 to 30 per cent iron-bearing materials, such as mill scale, and the mixture is slightly moistened. The charge is fed onto the grate of a sintering machine so that the material forms a bed 250 to 350 mm deep. A burner fired with gas or liquid fuel heats the top layer of the bed to 750-850°C. The grate is placed over chambers in which an exhaust fan builds up a vacuum. As a result, air is sucked through the bed of charge from the top to the bottom. The combustion initiated in the top relatively thin layer propagates downwards, towards the grate (Fig. 33), and the products of combustion are removed through the openings in the grate.

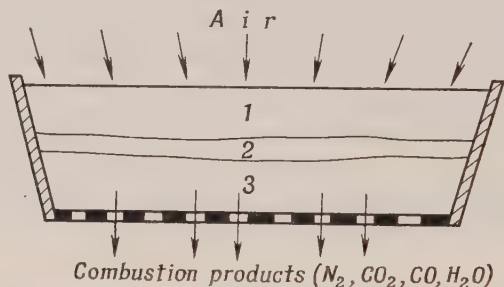


Fig. 33. Ore sintering on a stationary grate:

1—cooling zone; 2—fuel-burning and sintering zone; 3—preheating zone

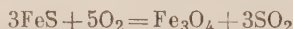
The combustion raises the temperature inside the charge to 1300-1600°C, depending on the amount of fuel burned and the rate of air flow through the charge. The magnetite is reduced in the presence of silica to fayalite ($2\text{FeO} \cdot \text{SiO}_2$ or Fe_2SiO_4) according to the reaction:



Fayalite melts at 1209°C. Therefore, a liquid phase forms in the combustion zone, wetting the unmelted grains of the charge. The fayalite forms eutectics with the ferrous oxide and silica, and the quantity of the liquid phase increases.

In solidifying, the molten silicates bind the charge particles together into a strong sinter.

Sintering removes much of the sulphur present in the ore material. In the case of iron ores, almost all of the sulphur is removed by sintering, according to the reaction:



When some limestone is added to the charge, the resulting product is a fluxed sinter which requires less flux when smelted in

a blast furnace. In the Soviet Union, practically all sinter is fluxed.

A travelling-grate sintering machine (Fig. 34) is, in fact, a moving belt consisting of separate pallets on which the charge is sintered. The travelling grate makes the bottom of the pallets. The pallets make up a sort of trough. The bedframe carries rails on which the

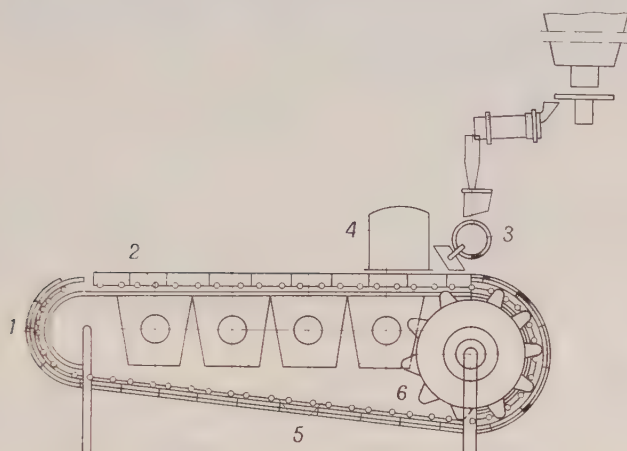


Fig. 34. Diagram of a travelling-grate sintering machine:

1—bedframe; 2—pallet; 3—feeder; 4—igniter; 5—vacuum chambers; 6—drive

pallets ride. Mixed and moistened, the charge is fed from a hopper onto the pallets. As they move on, the charge passes beneath an igniter which sets fire to the material. Simultaneously, a stream of air is sucked through the charge. When a pallet leaves the zone of the vacuum chambers, the material has already been sintered. At the end of the machine the sinter is dumped onto a screen and into wagons. The empty pallets ride on the bottom rails by gravity to the charging end of the machine where the teeth of two lifting wheels engage them by the trunnions and lift them onto the top rail track.

The capacity of a sintering machine depends on the area of the travelling grate or the area through which air is made to pass. The sintering operation lasts 15 to 20 minutes. The daily capacity of a sintering machine with an area of 50 sq m is up to 2200 tons of sinter. Currently, machines are being built with an area of 75 sq m to 200 sq m.

Prior to smelting lean ores have to be finely ground. Finely ground ores are very difficult to sinter. Therefore, a new technique of agglom-

eration known as pelletising, has been developed. It boils down to the following: the fine ore or finely ground concentrate is mixed with finely divided lime. The moistened charge is fed into a pelletiser which is a steel-plate cylindrical tank 300 to 400 mm deep and up to 4 m in diameter (see Fig. 102). The tank is set up at an angle of about 45° and rotates at 12 to 20 revolutions per minute. As the tank rotates, the moistened charge is rolled into pellets which can be made 10 to 50 mm across. The pellets thus obtained are sintered on travelling-grate machines.

14. Blast-furnace Fuel

In the Soviet Union, about 99 per cent of all pig iron is smelted with coke. Charged into a blast furnace in a mixture with iron ore or sinter, the coke burns with the oxygen of the blast, producing gases, mainly carbon monoxide which reduces the iron mineral to metallic form. The heat of coke combustion melts the iron and slag.

Down the blast furnace the coke has to withstand the pressure of the overlying material. For this reason, it should be sufficiently strong mechanically. It should also be in lumps so that the air and gases may be free to pass through the charge with high velocity. Finally, it should be porous for the chemical reactions to proceed at high rates.

Coke is produced by heating coal in air-tight retorts to such a temperature that the volatile constituents are driven off.

Coke of good quality is porous and has a silver-grey colour. The quality of coke is assessed on the basis of chemical analysis showing how much moisture, sulphur, volatile matter and ash is contained in it. The physical properties of coke are determined by tests for strength, porosity and resistance to abrasion. The content of sulphur and phosphorus, both detrimental impurities, must be kept to a minimum in a good quality of coke.

Usually coke contains 80-86 per cent carbon, 2-6 per cent moisture, from 0.4-0.7 per cent sulphur (the best grades) to 2 per cent sulphur (sulphurous coke), up to 15 per cent ash, and 0.7 to 2.5 per cent volatile matter. The heat value of coke is anywhere between 6500 and 7000 kcal/kg. Coke is usually crushed to a lump size of not less than 25 mm.

Of late, some of the blast furnaces have changed over from coke to natural gas. Natural gas is a mixture of hydrocarbons. The carbon in them burns to carbon monoxide and the hydrogen to water vapour. The burning of natural gas effects a considerable economy of coke, which is an expensive material. The burning of the hydrogen

to water vapour and the dissociation of the latter equalise the temperature throughout the furnace, thereby eliminating local overheating. The increased hydrogen content in the blast-furnace gas speeds up the rate of reduction.

15. Fluxes

In addition to the ore and fuel, fluxes normally are an important part of a blast-furnace burden. Their purpose is to convert the gangue of the ore and the ash of the coke into a fluid slag. Their nature depends on the composition of the material to be fluxed.

The sulphur that finds its way into the charge (mostly with the coke) can be withdrawn into the slag by limestone which forms basic slags.

Limestone (CaCO_3) must be in lumps measuring about 80 mm across. Limestone of good quality should contain not more than 1 per cent of both SiO_2 and Al_2O_3 . In poor limestone their content rises to 5 per cent. The sulphur and phosphorus content usually is low.

In the case of an aluminiferous gangue, acid slags should be formed, and the fluxes then are quartz, quartzite, sandstone or flint pebble.

Recent practice has been to incorporate some flux in the sintered product.

16. Description of a Modern Blast Furnace

A blast furnace is a tall cylindrical structure consisting essentially of a foundation, furnace bottom, hearth, bosh, stack, and top.

The foundation, of reinforced concrete, is partly underground and partly above the ground line (Figs. 35 and 36). It has to be sufficiently strong to carry the weight of the entire structure and burden (about 7000 tons for a volume of 1280 cu m).

The furnace bottom, made up of several tiers of firebrick 4 to 5 metres high (Fig. 36), stands on the foundation.

The hearth is that part of the blast furnace where molten metal and slag are accumulated and tuyeres are located (Figs. 35 and 36). The hearth (also known as the crucible) is of brickwork up to 1.5 m thick (in modern furnaces) surrounded by a heavy jacket of segmental cast-iron plates 30 to 36 mm thick. Like the bottom, the hearth is laid of high-quality firebrick, though current practice also favours carbon blocks.

The bosh is the hottest part and forms the zone of fusion. In modern blast furnaces, the bosh is of thin brickwork (Fig. 36), usually one brick thick (345 mm), in which case it is cooled by

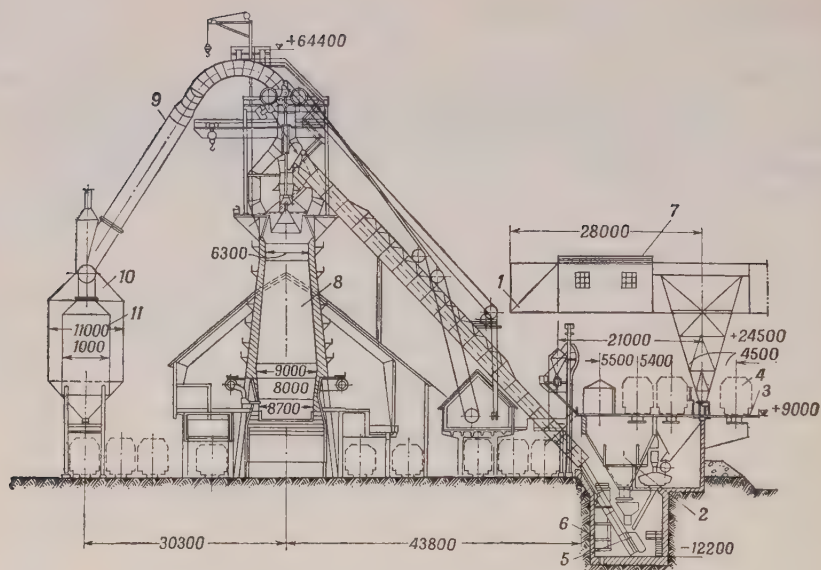


Fig. 35. Layout of a blast-furnace plant:

1—ore crane; 2—ore and flux bin; 3—bin bridge; 4—scale car; 5—skip car; 6—skip pit; 7—skip hoist house; 8—blast furnace; 9—downcomer; 10—1st dust catcher; 11—2nd dust catcher

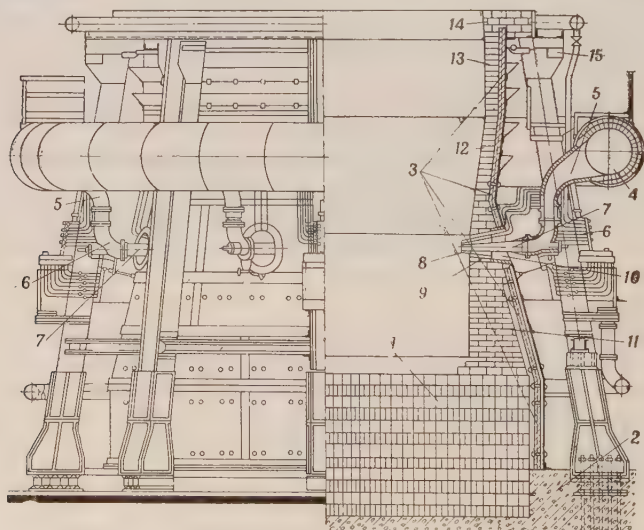


Fig. 36. Hearth and bosh of a modern blast furnace:

1—hearth bottom; 2—foundation; 3—cooling plates; 4—bustle (or blast) pipe; 5—fixed goose-neck pipe; 6—movable goose-neck pipe; 7—nozzle; 8—tuyere; 9—bronze cooler; 10—cast-iron tuyere cooler; 11—hearth; 12—bosh; 13—parallel bosh (or cylinder); 14—stack; 15—mantle ring

segmental castings and several rows of "bosh plates" through which water is circulated and which are set in the brickwork; the whole of a thin-walled bosh is enclosed in a shell. The intensive cooling of a thin-walled bosh forms a layer of solidified slag mixed with graphite on the lining. This layer protects the brickwork from the molten products of smelting.

The stack or shaft (Fig. 35) extends from the bosh to the top and is of riveted or welded steel-plate construction, lined with firebrick. The stack carries the top and is in turn set up on a "mantle ring" which is supported by columns. Two-thirds of the stack's height is cooled by a plate jacket.

The top (Fig. 37) is the place where the charge is fed into the stack through a charging apparatus and near which the top gases are withdrawn.

The brickwork of the top is protected against impacts of the charge with several rows of segmented steel bands.

The charging apparatus, known as the double-bell-and-hopper, or the cup-and-cone, consists of a small bell supported by a sleeve and fitting closely to the receiving hopper, and a large bell attached to the rod passing through the sleeve of the small bell. The large bell is made fast to the flange of the top ring. The receiving hopper consists of a stationary and a revolving part. The latter rotates together with the small bell through an angle each time a charge is dumped onto the small bell. In this way, the charge is uniformly spread all the way round the circumference of the stack. The bells are lifted and lowered by rocker arms connected with the bell sleeve and the rope of a hoist.

The top gases are withdrawn from the blast furnace by four symmetrically arranged off-takes. Much of the flue dust carried away in the gases falls back into the stack owing to the fact that the off-takes have very high risers (20 m). The risers are fitted at their highest points with explosion or relief valves to discharge excess gas into the atmosphere. These valves operate automatically, should the pressure of the top gases rise too much (due to the shock of a burden slip). The four gas risers converge into two mains which merge into a single downcomer which conveys the top gases into a dust catcher (Fig. 35).

Some 500 mm above the bottom of the hearth there is a taphole, called the iron notch, for tapping off the molten pig iron from the furnace. Below the iron notch is formed a "dead layer" of metal, known as the salamander, which protects the hearth bottom.

The iron notch is reinforced by a frame and a heavy cooler casting, called the dam plate.

Just below the tuyeres, 1.4 to 1.9 metres above the hearth bottom, are cinder or slag notches through which the slag is flushed.

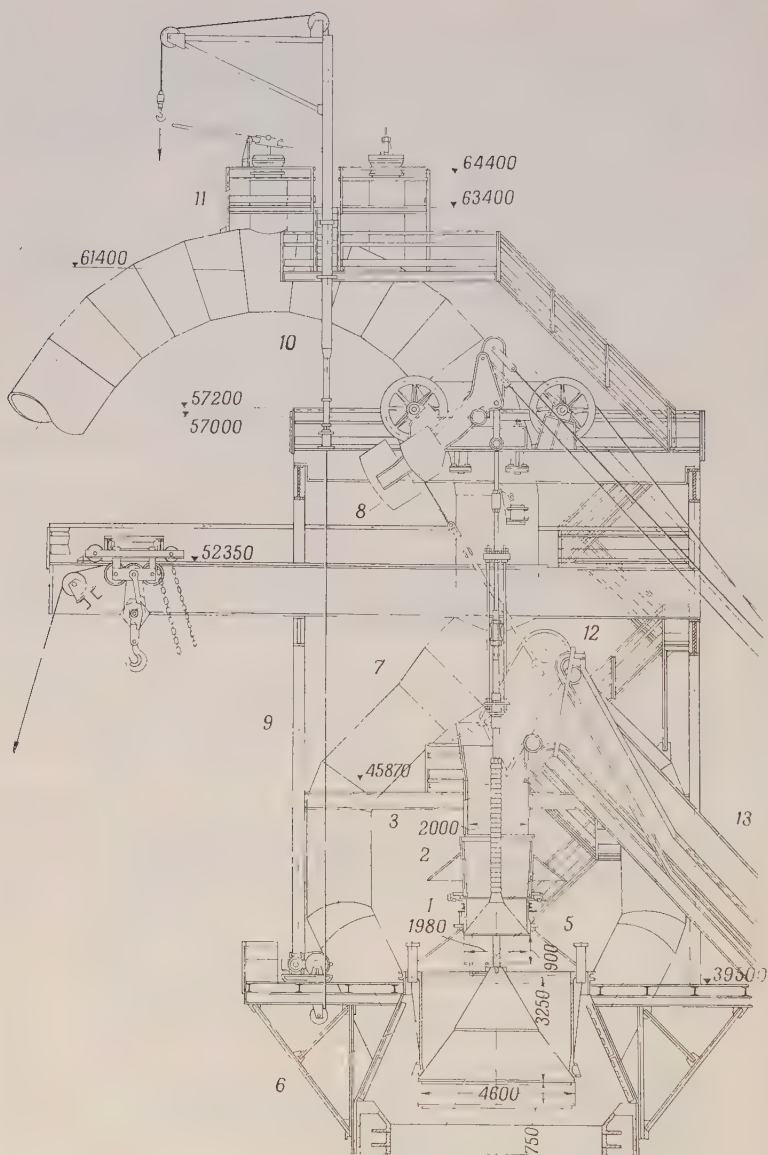


Fig. 37. Top arrangement of a modern blast furnace:

1—small bell; 2—small bell hanger; 3—small bell hopper; 4—large bell; 5—large bell hanger; 6—large bell hopper; 7—charging hopper; 8—hopper counterweights; 9—gas off-takes; 10—downcomer; 11—explosion or relief valves; 12—skip; 13—incline

A cinder notch consists of a water-cooled copper nozzle, called the monkey, with a tapering orifice 65 mm in diameter. The monkey fits into a tapering copper monkey or intermediate cooler which in turn fits into a cast-iron cinder cooler with a coiled tube. Between flushings the cinder notch is closed by an iron plug known as the bott.

Hot air for the blast is supplied by the hot-blast main from the hot-blast stoves. The main is connected to a large pipe encircling the furnace and called the bustle pipe. From the bustle pipe the blast is blown through the firebrick-lined goose-neck, the tuyere stock (also known as the leg pipe, boot leg or pen stock), the cast-iron blowpipe (sometimes called the belly pipe), and the tuyere (Fig. 36).

The diameter of a tuyere is 175 to 200 mm (for large furnaces) and its end projects into the furnace just enough to carry the blast away from the lining. The tuyeres are inserted into cast-bronze intermediate coolers and the latter fit into cast-iron tuyere coolers.

Hot-blast Stoves and Blowers. At present, the most efficient blowers for blast furnaces are turboblowers. A turboblower (Fig. 38) is a multistage centrifugal compressor with rows of blades seated on a common shaft. In rotating, the blades force the air towards the periphery, thereby compressing and driving it into a next stage. For a blast furnace to operate normally, the blast should be 2.2 to 2.6 normal cubic metres of air per minute per cubic metre of furnace volume.

Powerful blowers deliver 4000 to 4300 normal cubic metres of air per minute. The combustion of one ton of coke requires about 2880 normal cubic metres of blast.

In Cowper stoves the air blown into the furnace is preheated to 700 C. Modern furnaces, using the hot blast, require that the air be heated to 1000°C or higher.

A stove (Fig. 39) is a shell 30 to 50 m high and 8 to 10 m in diameter, welded or riveted from steel plate 10 to 14 mm thick. The shell is lined with two rows of firebrick, though high-temperature stoves use high-alumina brick. Inside the shell is divided into a combustion chamber and a heat-absorbing (checkerwork) chamber. The latter is packed with firebrick checker bricks. The checkerwork is set up on a substantial cast-iron grid supported by cast-iron columns.

The cleaned blast-furnace gas is mixed with the requisite quantity of air and is fed into the combustion chamber by a burner. The products of combustion pass upwards, turn back at the dome, and descend through the checkerwork, giving up heat to it. Cooled to 150 or 200 C, the gas is withdrawn from beneath the checkerwork, via the flue and into the funnel. After the dome is heated to

1100-1200°C, the gas and air supply is cut off, and the cold blast is passed through the checkerwork in the opposite direction. In a high-temperature stove the blast has to be heated to 1200°C; therefore, the dome of the stove is heated to 1400°C.

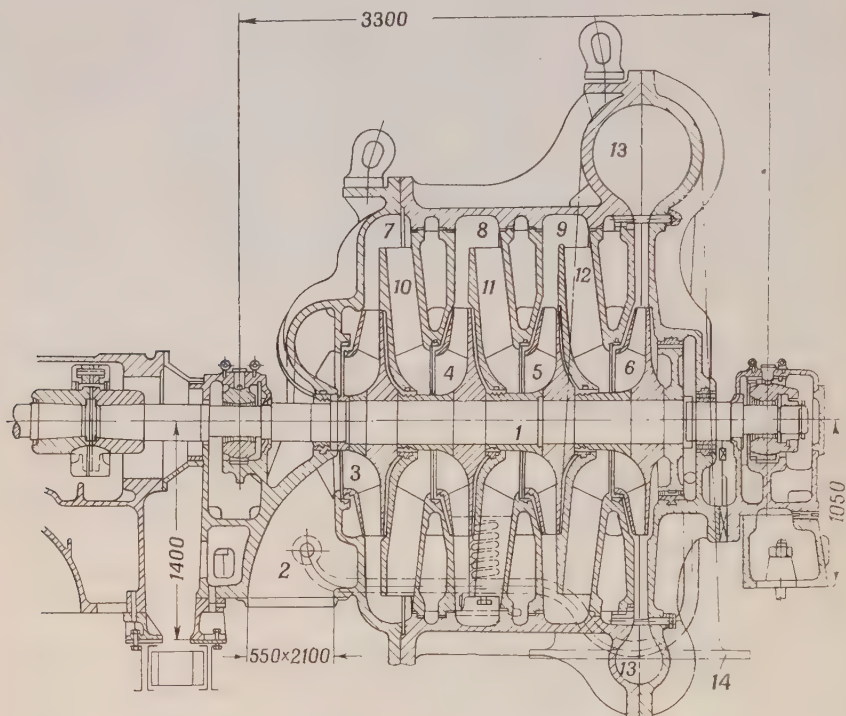


Fig. 38. A sectional view of a turboblower:

1—shaft; 2—suction port; 3, 4, 5, and 6—first, second, third- and fourth-stage impellers; 7, 8, and 9—diffusers; 10, 11, 12—fixed vanes; 13—volute; 14—discharge port

The size and number of hot-blast stoves per blast furnace depend on the size of the blast furnace they serve. The heating area of a stove for a furnace of 1513 cu m in volume is 30,000 sq m. In order to increase the heating area, to improve heat exchange, and to maintain the desired velocity of the gas and air, the checkerwork is sometimes laid in three tiers, differing in the diameter of openings in the checker bricks. Unfortunately, a three-tier checkerwork is difficult to clean. For this reason, the stoves currently being built in the Soviet Union have a single checkerwork with cells measuring 60 mm square, laid in brick 50 mm thick.

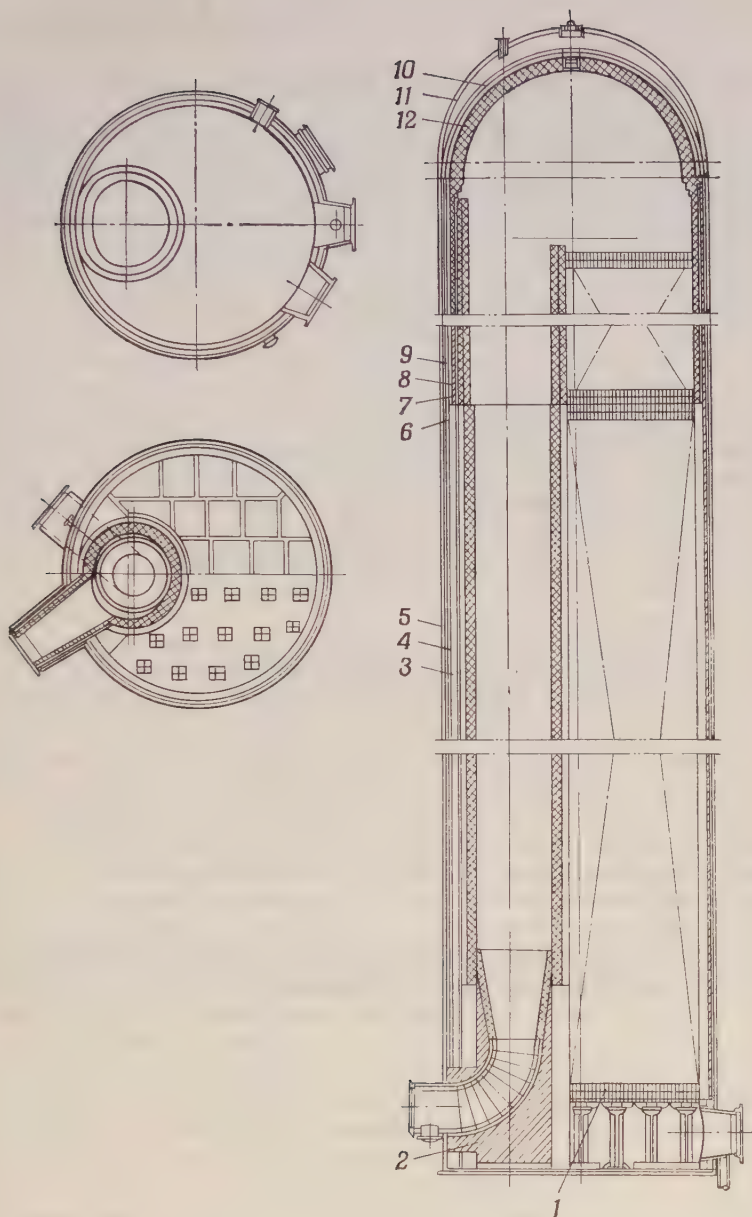


Fig. 39. Hot-blast stove:

1—heat-resistant iron grid supporting checkerwork; 2—flameproof concrete; 3—fire-brick, 345 mm; 4—tripoli brick, 65 mm; 5—firebrick-asbestos filling, 60 mm; 6—high-alumina brick, 230 mm; 7—light-weight brick, 113 mm; 8—firebrick-asbestos filling, 62 mm; 9—tripoli brick, 65 mm; 10—same, 123 mm; 11—light-weight brick, 113 mm; 12—high-alumina brick, 450 mm

17. Accessories to the Blast Furnace

Blast furnaces with a useful volume of 1513 to 2286 cubic metres produce 2000 to 3800 tons of pig iron a day, for which purpose they consume 4000 to 7000 tons of source materials. Trouble-free operation in such circumstances is only possible with complete mechanisation of all work.

The materials arriving at an iron works (iron ore and limestone) are unloaded into a trench from which an ore bridge transfers them onto the stock yard. On the stock yard the materials are averaged into a stock pile of uniform composition throughout. Averaging improves furnace working. Also the capacity of the furnace is utilised more fully and much fuel is saved. The same advantage can also be derived by suitably arranging materials-handling facilities. The materials from the stock piles should be taken by special charge-loading machines at the end and the full depth of a pile.

From the stockyard the materials go through a sintering plant and then into bins arranged inside a concrete platform running along the blast furnaces. Instead of the ore bridge which travels along the bins slowly, the latter can be loaded by a transfer-car which rides a rail track above the bins and discharges the materials through the bottom.

The bins hold as much sinter or ore as is necessary for a furnace to operate for 48 to 60 hours, and limestone for 32 to 48 hours.

From the bins the materials are unloaded into a scale car which is a motor-driven dump-car with a weighing mechanism, riding a rail track between and beneath the bins. The operator fills the respective pockets of the car with the requisite materials and transfers them into a skip car which hauls and automatically dumps the charge into the furnace. At some iron works, the materials are proportioned automatically.

Placed on either side of the skip pit are coke bins holding as much coke as is necessary for the furnace to operate for 8 to 12 hours. Coke is loaded into the skip car through a roller screen, which eliminates coke fines, and a coke weigh hopper.

All the mechanisms handling the ore, limestone and coke are automatically interlocked to exclude any wrong sequence of operations. Automatic interlocking makes it possible for a single man (the skip-hoist operator) to run the whole set-up or for the entire machinery to be computer-controlled.

Iron and Slag Handling. The foundry yard is a sheltered site with iron and slag spouts or launders laid on it. After a tap of iron, the iron notch is made up with refractory clay by an electric- or air-operated tap-hole gun, also known as the mudgun. The iron notch is opened by a drill or an air hammer.

Molten pig iron is poured into ladles lined with grog brick and holding 80 to 100 tons.

In the case of integrated works, the iron is ordinarily taken in these ladles to a steel-making shop where it is poured into a mixer, a firebrick-lined, heated receiver of 600 to 2000 tons capacity. The mixer averages the composition of pig iron obtained from different taps and forms a stock of uniform molten metal for the steel plant.

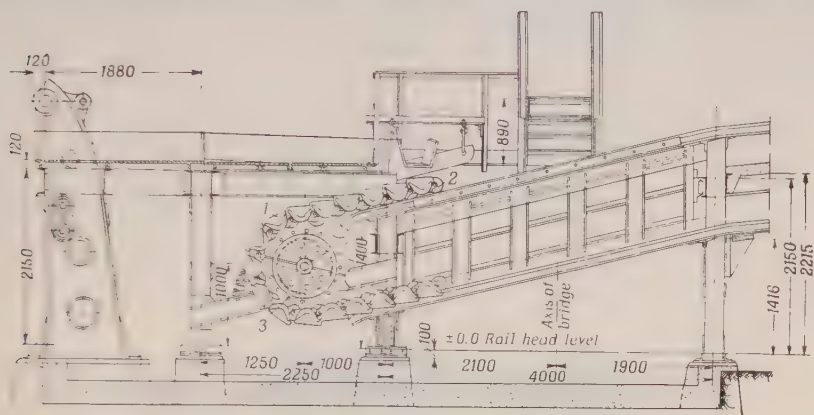


Fig. 40. Pig-iron casting machine (view from the pouring side):
1—moulds; 2—rollers; 3—sprocket

Foundry pig iron is handled by a pig-casting machine. Fig. 40 shows a pig-casting machine as viewed from the pouring end. It is an endless conveyor carrying cast-iron moulds hinged together by rollers which move in guides. The molten pig iron from a ladle flows down a spout and into the moulds. The lower driving wheel of the machine rotates clockwise. Its teeth engage the mould rollers in turn, and the entire conveyor is set into motion (on the upper guides from left to right).

The rate of cooling (with water) and speed of the conveyor are so chosen that by the moment a mould arrives at the end of the machine, the pig iron in it has already solidified. When a mould goes over the drive head, the pig, weighing about 50 kg, drops out and slides down a chute onto a railway flatcar.

Slag is hauled in ladle cars to a dump or is run into a water-filled granulating pit to obtain granulated slag utilised in the manufacture of brick, cement, etc.

18. Cleaning of Blast-furnace Gas

Should the ore be prepared inadequately, the top (blast-furnace) gas will carry away much flue dust with it—up to 170 kg per ton of pig iron. The runaway of flue dust can be reduced by a factor of 3 to 5 by using the sinter and an increased top pressure. Yet, the top gas requires a thorough cleaning before it is burned in hot-blast stoves, if the burner and checkerwork are not to be choked up with dust. The requirements for gas purity increase with the complexity of stove design.

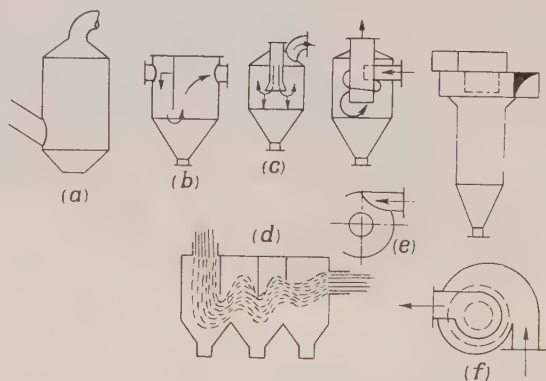


Fig. 41. Dry-gas cleaning apparatus:
(a) dust catcher; (b), (c), (d) inertia dust catchers; (e), (f) cyclones

In metallurgy, several methods of gas cleaning are employed: mechanical (dry and wet) cleaning, electrical precipitation, and filtration.

1. Dry mechanical cleaning is based on gravity and inertia. A dry dust catcher (Fig. 41a) is a settling chamber with a cross-sectional area several times larger than that of the pipeline bringing the gas. As it goes from the pipeline into the chamber, the gas slows down to a velocity which allows the particles to settle to the bottom of the chamber. The settled-out material is removed from the chamber at regular intervals. In some designs of settling chambers, such as shown in Fig. 41b, c and d, the gas is both slowed down and is made to change its direction abruptly. Due to inertia, the particles leave the gas stream and settle to the bottom of the chamber.

Of all inertia dust catchers, the cyclone type is the most efficient (Fig. 41e and f). In a cyclone the gas is passed tangentially to follow a spiral path at a velocity of 15 to 20 m/sec. Centrifugal force throws the particles against the cyclone wall where they are slowed

down by friction and settle into a hopper. Cyclones are capable of separating about 90 per cent coarse dust and 35 to 45 per cent fine dust. Better results are obtained with small-diameter cyclones, as this increases the centrifugal force acting on the particles.

2. Wet mechanical cleaning, or scrubbing, utilises the increase in the weight, size and adhesion of the particles when they are moistened. For better contact between the water and dust, the water is atomised by sets of sprays. The resultant mixture is a

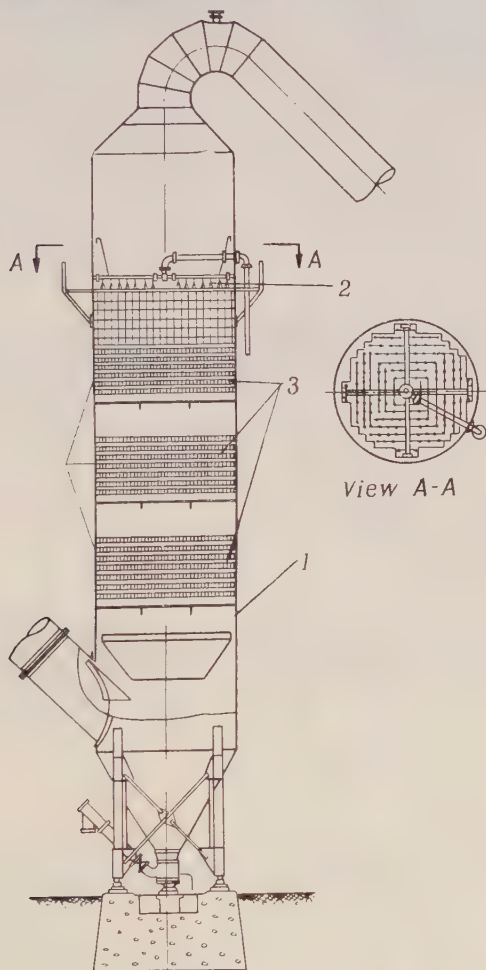


Fig. 42. Secondary gas scrubber;

1—scrubber shell; 2—sprays; 3—wood packing

suspension of solids in water. This method is utilised in stationary, or static, spray scrubbers, usually of the tower type, the gas passing upwards counter-currently to the descending water. The packing material in stationary spray scrubbers may be wooden grates, as shown in Fig. 42, hurdles, ceramic tiles, or metal spirals. Stationary scrubbers are used for primary (coarse) gas cleaning. Secondary (fine) gas cleaning is done in rotary, or dynamic, spray scrubbers. In them contact between the water droplets and the suspended matter of the gas is improved by mechanical agitation of the gas and water by means of vanes. The dust is thoroughly wetted and washed down by water.

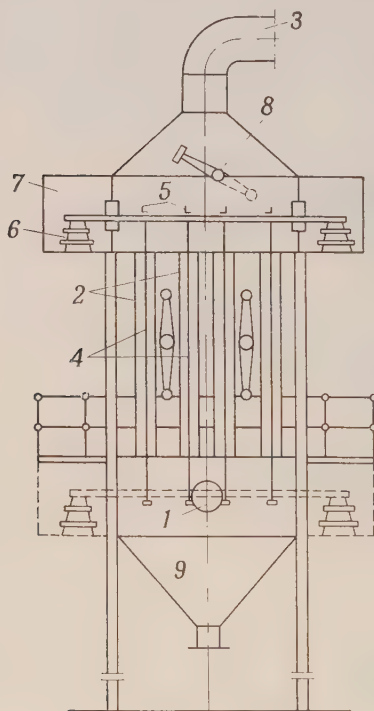


Fig. 43. Diagram of an electric precipitator:

1—gas line; 2—collecting pipe electrodes; 3—gas discharge; 4—ionising electrodes; 5—frame-work; 6—insulators; 7—side boxes; 8—rapping device; 9—bottom

3. Electrical precipitation (Fig. 43) is effected in a high-voltage direct-current electric field (50 to 100 kV) established by an ionising and a collecting electrode.

Ionising electrodes are made of wire 2 to 5 sq mm in cross-section. Collecting electrodes may be either plates (in which case each ionising electrode is placed between them); or pipes with each ionising electrode hung axially in the pipe. At the preset potential

difference, the gas is ionised, and the charged gas particles attach themselves to solid particles and the latter move towards the collecting electrode where they lose their charge and settle. Admission

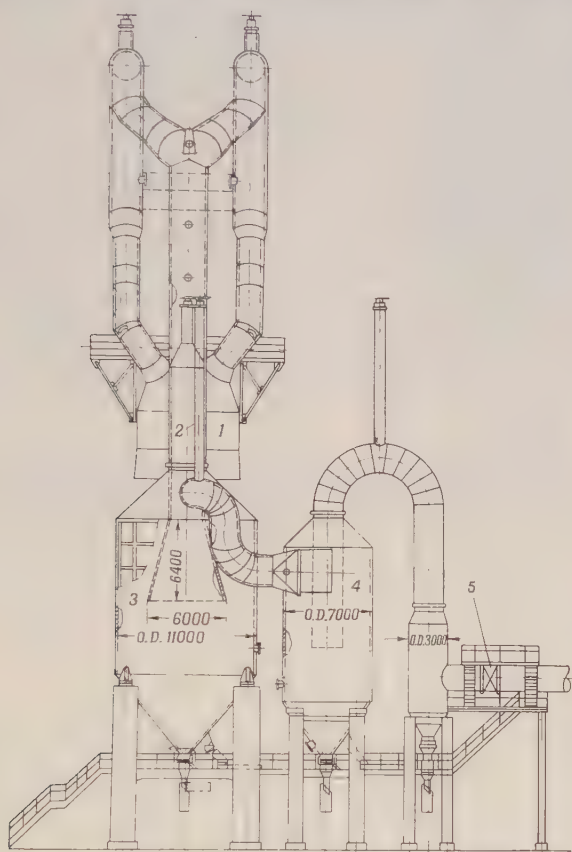


Fig. 44. Primary dust catchers:

1—blast-furnace top; 2—downcomer; 3—first dust catcher; 4—second dust catcher; 5—valve

of the gas is interrupted at regular intervals, and a rapping device shakes the plates (or pipes), causing the collected particles to fall into hoppers beneath.

The blast-furnace gas is usually cleaned in three stages: coarse (down to 4-1 gram of dust per cubic metre); semi-fine (down to 0.8-0.1 gram of dust per cubic metre), and fine (down to 0.05-0.01 gram per cubic metre).

Coarse cleaning is accomplished by two dust catchers placed in tandem (Fig. 44) where about 80 per cent of the dust is removed. The dust catchers are followed by a primary washer, which is a static spray scrubber, such as shown in Fig. 42, where the dust

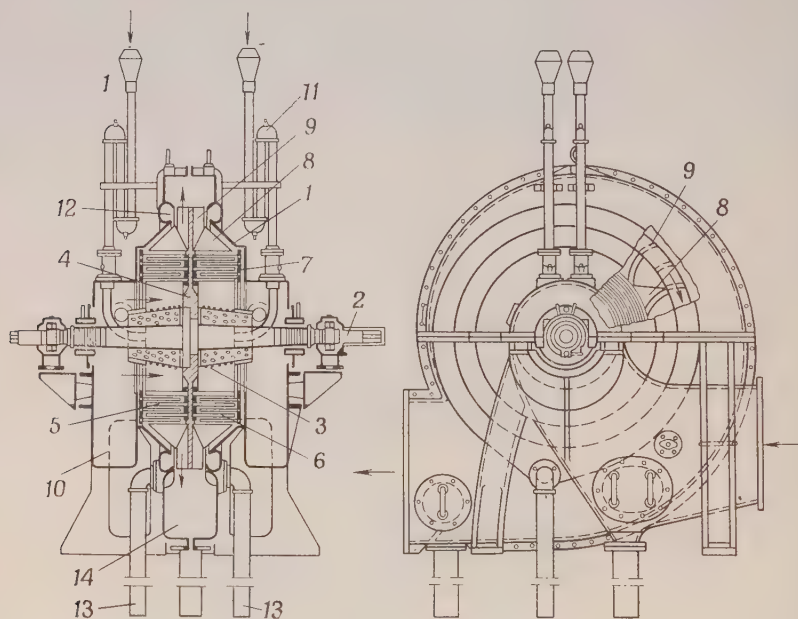


Fig. 45. Disintegrator (rotary spray scrubber):

1—shell; 2—shaft; 3—distributing cone; 4—disk; 5—movable radial bars; 6—stationary bars; 7—stationary bar rings; 8—scrubbing blades; 9—air impeller; 10—side inlets; 11—siphon pipes; 12—water outlet; 13—spent water discharge; 14—clean gas out

content of the gas is reduced to 0.8-0.2 g/cu m. Fine cleaning is done in rotary spray scrubbers (disintegrators) or electrical precipitators.

A disintegrator (Fig. 45) is a powerful fan sucking in the gas from a primary washer. Its shaft carries an impeller and radial bars or arms. In rotating, the movable radial bars pass between stationary radial bars or arms anchored in the shell. The rotating impeller entrains the gas from two side ports, and the radial bars mix it with the water continuously fed by siphon tubes. The wetted dust is thrown into a discharge passage, while the gas and water mist are driven by the impeller into the discharge hole of the middle chamber. The water droplets are forced onto the wall to flow down into a drainage pipe, while the cleaned gas leaves by a gas line.

An average disintegrator can clean 80,000 cu m of gas an hour. Using 0.5 to 0.6 litre of water per cubic metre of gas, it reduces the dust content of the gas to about 0.1 gram per cubic metre. With lower capacity and increased water flow rate, the cleanliness of the gas can be improved to 0.015-0.02 gram per cubic metre.

The final stage in blast-furnace gas cleaning may alternatively be accomplished in wet-process electroprecipitators (Fig. 46). The collecting electrodes are circular or hexagonal pipes 150 to 300 mm in diameter and 3 to 4 metres long. The ionising electrodes are wires hung axially in the pipes. The cleaned gas is withdrawn by a gas line located at the top of the unit. The water spraying the electrodes and the packing is collected in a settling tank. The capacity of such a unit is 40,000 cubic metres of gas an hour. The dust content is reduced to 0.07-0.2 g/cu m. The rate of water flow is 3.5 to 4 cu m, and power consumption is 0.55 kWh per 1000 cu m of gas.

19. Blast-furnace Reactions

Combustion of the Coke. The air for combustion of the coke enters the furnace through the tuyeres heated to a temperature of 600° to 850°C. In hot-blast furnaces the temperature of the blast is maintained between 925° and 1100°C. The carbon of the coke burns according to the reaction $C + O_2 = CO_2 + 94.03 \text{ kcal}$, with a slight excess of oxygen, thereby producing an oxidising atmosphere at the

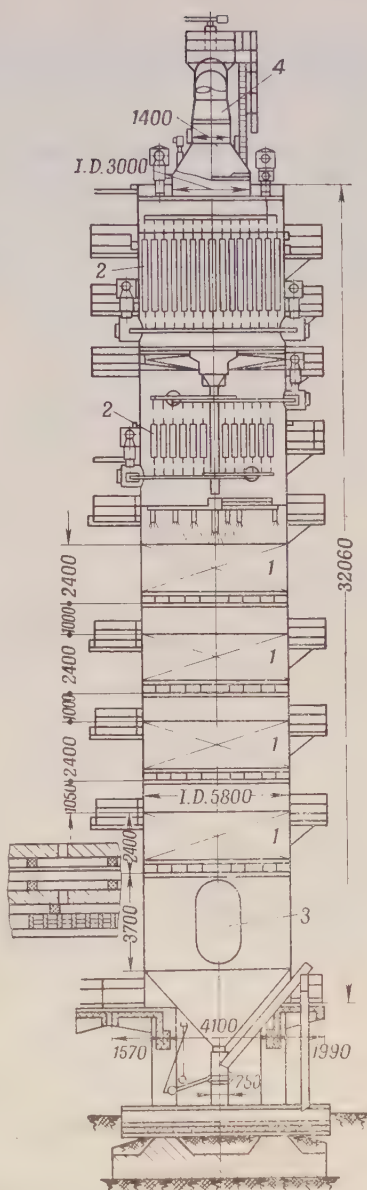
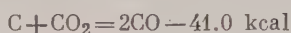


Fig. 46. Wet process electroprecipitator:

1—wet-process packing; 2—precipitator; 3—dirty gas inlet; 4—clean gas outlet

tuyeres. The carbon dioxide is then reduced by the carbon of the incandescent coke to carbon monoxide:



The chart in Fig. 47 shows how the composition and temperature of the gas vary in the combustion zone of the blast furnace. The oxidising zone in modern blast furnaces (over 1000 cu m in volume) extends for about 1200 mm from the tuyeres towards the vertical axis of the stack and for 600 to 1000 mm upwards. In the direction

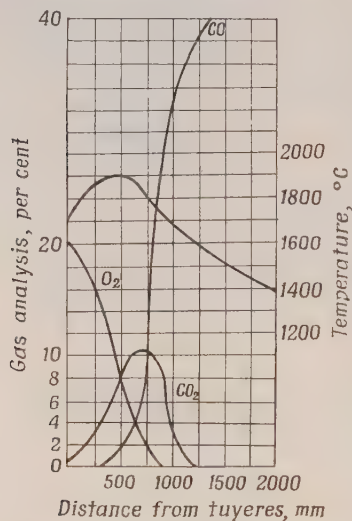
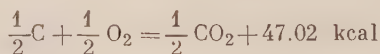


Fig. 47. Temperature gradients and variations in gas analysis with distance from the tuyeres

from the tuyeres to the axis of the furnace the oxygen content decreases and that of CO_2 first increases and then decreases, as the reaction $\text{C} + \text{CO}_2 = 2\text{CO}$ progresses.

The combustion of the coke in a blast furnace may be summed up as follows:



As the air blast usually carries some nitrogen, the gas composition in the hearth zone will be 34.7 per cent carbon monoxide and 65.3 per cent N_2 (by volume). The gas produced in the hearth zone rapidly ascends the stack, giving up heat to the burden materials and reducing them.

In burning at the tuyeres, the coke clears some space continuously at the upper level of the hearth and bosh, and the column of solid materials gradually descends.

The hottest temperature in a blast furnace is obtained at the focal point of combustion which lies within 700 or 800 mm of the tuyeres. For conversion pig iron, the hottest temperature is 1850°C and for ferrosilicon 2000°C. The temperature of the gas at the top usually is 250 to 275°C.

The pressure of the blast at the tuyeres increases with the size of the furnace. For blast furnaces with a volume of 1000 cu m it is about 2.2 atm (abs). Towards the top the pressure gradually drops, being 1.1 atm (abs) at the stockline.

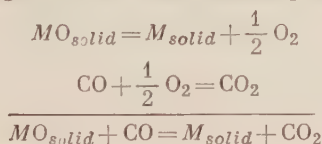
A recent development in blast-furnace operation has been to use an increased top pressure. This is accomplished by inserting a throttling or septum valve in the gas off-take to restrict the effective passage, and so the pressure of the top gas rises to 1-1.8 atm (gauge).

The increased pressure of the top gas reduces the velocity of gases through the stack column, thereby increasing the time of gas/solid contact. Furthermore, the gas is distributed more uniformly over the cross-section of the burden, making it possible to increase the flow rate of the air blast and, owing to this, to increase furnace productivity per unit capacity by as much as 10 per cent or even more. Another advantage of the lower velocity of the gas as a result of the increased top pressure is a decrease in the loss of flue dust (35-40 instead of 120-140 kg of dust per ton of pig iron).

Reduction of the Iron Oxides and Other Compounds. In Russia, the basic mechanism of reduction has been studied by Baikov who has established the principle of consecutive transformations. Under this principle, Fe_2O_3 , the highest oxide of iron, is gradually reduced to metallic iron. The sequence of reduction of the iron oxides depends on the difference in the strength of bonds between the atoms of oxygen and iron. The affinity of iron oxides for oxygen increases as follows:

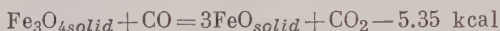
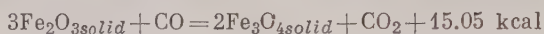


The thermodynamic possibility of a reduction reaction (according to Baikov) is determined by two partial equations: the dissociation of the oxide with the evolution of oxygen, and the combination of the oxygen with the reducing agent:



Reduction is thermodynamically feasible if the affinity of the reducing agent for oxygen is greater than that of the metal. If the affinity is the same, an equilibrium state is attained.

The reduction of iron oxides by carbon monoxide proceeds as follows:



At temperatures below 572°C, ferrous oxide is unstable. Therefore, the magnetic iron oxide is reduced directly to metallic iron according to the reaction:



The equilibrium state of reduction reactions may be attained at a given temperature only at a definite ratio of the partial pressures $\left(\frac{p_{\text{CO}}}{p_{\text{CO}_2}}\right)$ or of molal concentrations $\left(\frac{\text{CO}}{\text{CO}_2}\right)$ in the gaseous phase.

Fig. 48 shows an equilibrium diagram for iron, carbon and their oxides based on numerous investigations.

The curves in the diagram relate the equilibrium ratios $\frac{\text{CO}}{\text{CO}_2}$ of the respective reactions to temperature.

The equilibrium curves bound the fields within which the temperature and composition of the gaseous phase are such that the respective solid phase is stable.

The upper field determines the conditions for the stable existence of metallic iron. Obviously, when the $\frac{\text{CO}}{\text{CO}_2}$ ratio is greater than is necessary for an equilibrium at a given temperature, iron oxides are reduced to metallic iron. Increasing the content of carbon monoxide in the gaseous phase moves the whole system farther away from the equilibrium, thereby promoting reduction.

The composition of the blast-furnace gas is far from the state of equilibrium in all of the furnace zones. Owing to high velocity, the gas leaves the furnace with much of its carbon monoxide remaining unused. The ratio of CO to CO₂ at the top usually is 2 or 3.

The temperature at the top is high enough to reduce the iron oxides immediately below the throat. The bulk of the oxides, however, is reduced to metallic iron at the lower end of the stack and in the cylinder (also known as the belly or parallel bosh) (Fig. 49).

Chufarov and co-workers (U.S.S.R.) have experimentally proved that the reduction mechanism is autocatalytic adsorption which proceeds in three stages: (1) the reducing gas (CO or H₂) is adsorbed on the surface of the oxide, MO; (2) the oxygen breaks away from

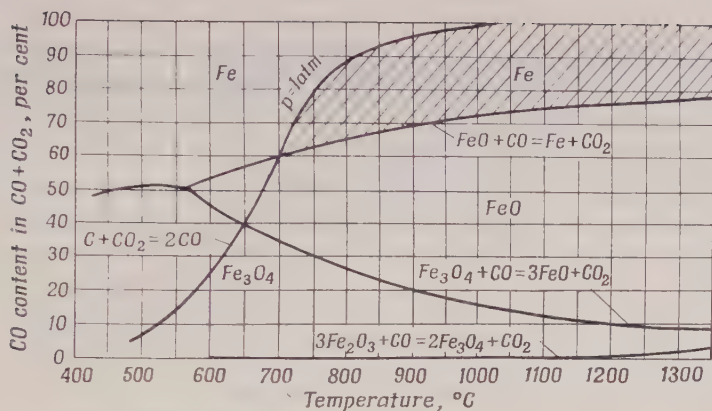


Fig. 48. Equilibrium diagram for iron and its oxides, carbon, and a gaseous phase consisting of CO and CO₂

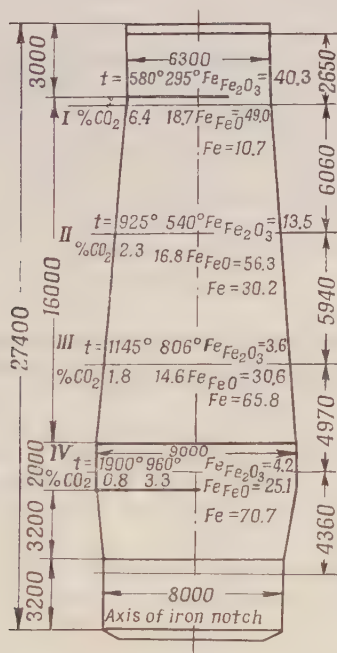
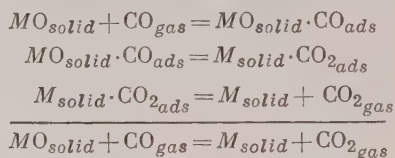


Fig. 49. Zones of reaction in a blast furnace

the oxide and attaches itself to the adsorbed molecules of CO or H_2 to form molecules of CO_2 or H_2O and a new phase, M ; (3) the product of reduction, CO_2 or H_2O , is desorbed from the reaction surface:



The autocatalytic reduction of iron oxides is characterised by low rate of reaction in the beginning due to some difficulty with which a new phase is formed; intensive reduction in the second stage when the new phase is growing around the noduli of crystallisation (the rate of interaction increases as the area of the interface between the solid phases increases); and a decrease in the rate of reactions in the third stage due to the fact that the many reaction zones merge into a single one, and its area is gradually reduced as the reaction proceeds.

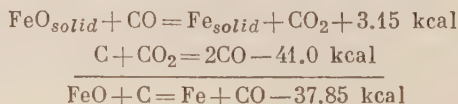
The rate and extent of reduction of iron ores are governed by the rate of supply of the reducing gas to the reaction zone and the rate of withdrawal of the resultant gases from it; the temperature of the process (the velocity of reaction increasing with temperature); the particle size of the ore or sinter (the velocity of reaction increasing with decreasing size, due to the increase of the area of contact); the porosity of the ore and sinter (reduction being facilitated and speeded up by increasing porosity).

An increase in the pressure of the reducing gas causes more of it to be adsorbed on the surface of the ore particles, while an increase in the velocity of the reducing gas acts in the opposite direction.

Iron oxides can also be reduced by solid carbon, a process called direct reduction, as distinct from indirect reduction by carbon monoxide.

The extent of direct reduction is, however, insignificant for several reasons. The area of contact between the ore and coke is small and the reaction ceases as soon as the ore particles are enveloped by a thin layer of reduction products, and diffusion between solid phases is a very slow process.

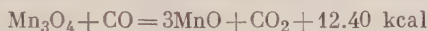
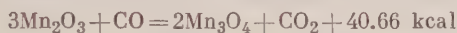
According to Baikov and Stark (U.S.S.R.), direct reduction should be construed as a double reaction of the reduction of iron oxide by carbon oxide and a reaction of carbon dioxide with carbon:



The two partial reactions and, consequently, their aggregate reaction can only proceed under conditions corresponding to the cross-hatched area of the diagram in Fig. 48. For direct reduction to be possible, the carbon dioxide must transform to carbon monoxide at a rate sufficient to make up for the carbon monoxide spent to reduce the ore. Therefore, the extent of direct reduction increases with rising temperature. In the blast-furnace zones with a temperature of 900-1000°C or more, the ferrous oxide is reduced solely by the direct process.

In smelting ordinary grades of pig iron, some 40 to 60 per cent of iron is reduced directly. In smelting pig iron high in manganese and silicon, direct reduction accounts for as much as 80 per cent of the total for the reason that the oxides of silicon and manganese can only be reduced directly.

Manganese oxides are introduced into the charge with the iron and manganese ore and are reduced much as the iron oxides are:

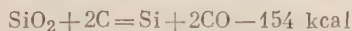


The first three oxides are easy to reduce. The large quantities of heat liberated in the process are not utilised, as the reactions take place near the top of the furnace. For MnO to be reduced, the ratio $\frac{p_{\text{CO}}}{p_{\text{CO}_2}}$ must be higher than in the case of ferrous oxide. Therefore, MnO is mainly reduced in the high-temperature zone by carbon:



It takes twice as much heat to reduce one unit of manganese than one unit of iron. Therefore, in ferromanganese production the consumption of coke is 2.2 to 2.5 weight units per unit weight of the alloy. The reduction of manganese can be facilitated by adding more fuel and using a hot blast. Another important requirement is the use of basic slags, as in the case of acid slags much of MnO transforms to silicates from which manganese is difficult to reduce. Losses of manganese can be reduced by reducing the quantity of slag.

A still greater ratio of p_{CO} to p_{CO_2} is required in the gas for the reduction of silicon because of its greater affinity for oxygen. Silica is mainly reduced by solid carbon at high temperature:

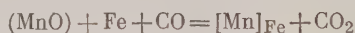


The reduction of silica is facilitated by high-melting silicious slags when charcoal is used as the fuel, and by high-melting aluminiferous slags when coke is used. High-melting slags are essential

if a sufficiently high temperature is to be maintained in the crucible zone.

The high temperatures necessary for the production of silicon iron can be obtained by increasing the amount of fuel fed into the furnace and by using a very hot blast.

The reduction of MnO , SiO_2 , etc., in the blast furnace is considerably facilitated by the fact that the reduced product (manganese or silicon) dissolves in the iron. When the resultant manganese dissolves in the iron, the ratio of p_{CO_2} to p_{CO} necessary for the reduction of MnO is lower than it should be when the manganese does not dissolve in the iron:



$$K_p = \frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{p'_{\text{CO}_2} [\text{Mn}]}{p'_{\text{CO}} [\text{Mn}]_{\text{saturation}}}$$

The value of K_p is the ratio of p_{CO_2} to p_{CO} for the reduction of pure MnO to pure Mn . Then:

$$\frac{p_{\text{CO}_2}}{p_{\text{CO}}} = \frac{p'_{\text{CO}_2} [\text{Mn}]}{p_{\text{CO}} [\text{Mn}]_{\text{saturation}}}$$

hence:

$$\frac{p'_{\text{CO}_2}}{p'_{\text{CO}}} = \frac{p_{\text{CO}_2} [\text{Mn}]_{\text{saturation}}}{p_{\text{CO}} [\text{Mn}]}$$

and consequently:

$$\frac{p'_{\text{CO}_2}}{p'_{\text{CO}}} > \frac{p_{\text{CO}_2}}{p_{\text{CO}}}$$

In other words, the reduction is easier to accomplish even with a smaller content of carbon monoxide in the gas when a solution of manganese in iron is formed than when it is not. This principle underlies the production of manganese, chromium and silicon alloys of iron.

The reduction of oxides which are difficult to reduce is likewise facilitated by the formation of the respective carbides.

Phosphorus into the blast furnace is introduced mainly as part of the minerals $\text{Ca}_3\text{P}_2\text{O}_8$ and $\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$. At high temperature and in the presence of coke these compounds are fully reduced. The reduction of phosphorus from calcium phosphate is facilitated by silica:

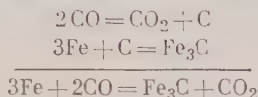


There is always much silica in the charge, compared with the calcium phosphate, and all of the phosphorus introduced into the furnace with the ore is reduced and enters the pig iron where it

forms iron phosphide (Fe_3P). Thus, the phosphorus content of pig iron is solely dependent on its quantity in the charge, and it can only be reduced by improving the quality of the source materials.

Oxides of nickel and cobalt can be reduced at a relatively low $\frac{\text{CO}}{\text{CO}_2}$ ratio in the gas. Therefore, all of the nickel and cobalt contained in the ore enter the pig iron.

Formation of Pig Iron. The reduction of the ore produces a mass of sponge iron which is carburised by carbon monoxide:



The carbon monoxide finds its way into the pores of the sponge iron, decomposes on the surface of the reduced iron, and the resultant carbon is absorbed by the metal. Carburised iron has a lower melting point. For example, the iron-carbon eutectic (4.3 per cent carbon) melts at 1130°C (Fig. 32). The carburised iron melts at the top of the bosh and drips between the coke lumps, picking up some more carbon.

The presence of carbide-forming elements in the pig iron (such as chromium, manganese, etc.) increases total carbon in it. On the other hand, silicon, phosphorus and sulphur which combine with iron decrease it. In addition to this, silicon promotes the decomposition of iron carbide (Fe_3C) and the precipitation of the carbon as graphite. This effect improves the mechanical properties of pig iron; therefore, foundry pig iron is smelted so as to have more silicon in it than in steel-making irons.

Slag Formation. Slag formation is a process by which the molten oxides of the gangue and the ash in the fuel combine with the flux oxides to form the blast-furnace slag.

The first drops of molten slag appear at the lower end of the stack and above the parallel bosh as low-melting eutectics. Its amount grows fairly rapidly as it dissolves oxides of iron and manganese, forming rather fluid low-melting silicates of iron and manganese. The slag at the lower end of the stack and on the top of the parallel bosh carries up to 20 per cent ferrous oxide. As it trickles down, the slag gradually loses much of its iron and manganese oxides through their reduction and picks up much lime instead, which fact raises its melting point.

The gangue of the iron ore usually carries some alumina (Al_2O_3). Alumina has a considerable effect on the melting point and fluidity of the slag. The absence of alumina in the gangue retards slag formation. In smelting foundry irons the ratio of SiO_2 to Al_2O_3 usually

is from 2 to 1.25; in smelting steel-making irons, the ratio is 2 and greater.

The slag has a direct bearing on the composition of the pig iron and furnace operation as a whole. Incidentally, the fusibility of the slag affects the temperature in the hearth zone. A gangue which melts at too low a point will arrive at the hearth with too little heat and reduce the temperature in the hearth. Conversely, a refractory gangue arrives at the hearth very hot, and its temperature rises.

Slag formation should always begin after the iron has been reduced and carbonised and the pig iron has begun to melt, and should complete in the belly or at the junction of the belly and the bosh.

The Behaviour of Sulphur in the Blast Furnace. In the iron ore and coke sulphur may be present as pyrite, pyrrhotite and stable sulphates. The pyrite is decomposed well before the pig iron is produced, and half of the sulphur is carried away in the gases. In the sinter sulphur is present as FeS and stable sulphates.

Most of the sulphur is introduced into the burden with the coke. When the coke burns, the sulphur is oxidised, forming SO_2 which is reduced by the carbon. The resultant gas combines with some iron and manganese and enters the pig iron.

The desulphurisation of the pig iron requires a basic slag and is effected when the molten metal drips through the bed of slag and at the interface between metal and slag, owing to the formation of calcium sulphide which is insoluble in the pig iron and soluble in the slag:



The solubility of sulphur in the slag increases with the temperature and the basicity of the slag, and with the reduction of its iron and manganese oxides contents, because the desulphurisation reactions are endothermic. The overheating of high-lime slags raises their fluidity and reactivity.

For a silica plus alumina ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) content of 45 to 55 per cent, the ratio of the sulphur in the slag to that in the pig iron will be anywhere from 20 to 40 per cent. For slags of high basicity, the ratio increases to 60-80 per cent.

20. Products of Blast-furnace Operation

Grades of Pig Iron. According to the classification adopted in the Soviet Union, all pig irons are divided into foundry, conversion or steel-making (open-hearth, Bessemer and Thomas), and special (blast-furnace ferroalloys used as deoxidisers in steel making).

Analyses of typical grades of foundry pig iron are given in Table 4. Owing to the increased silicon content, the carbon in foundry pig iron is mainly present in the form of graphite. For this reason, it shows a dark-grey structure which grows darker with increasing

Table 4

Analyses of Several Foundry Irons
(per cent)

Grade	Silicon	Manganese		Phosphorus				Sulphur	
		Group		Class				Category	
		I	II	A hema- tite, max.	B ordi- nary	C phos- phor- ous	D	I	II
								max.	
JK00	3.76-4.25	0.5- 0.9	0.91-1.3	0.4	0.11- 0.3	0.31- 0.7	0.71- 1.2	0.02	0.03
JK0	3.26-3.75								
JK1	2.76-3.25								
JK2	2.26-2.75								
JK3	1.76-2.25								
JK4	1.25-1.75							0.04	0.05

silicon. For its smelting, foundry iron requires higher coke ratios (1-1.2 tons per ton of pig iron), and a hotter blast.

Foundry iron should preferably be smelted from lean, easily reduceable ores with a silico-aluminiferous gangue which melts at a high temperature. The smelting time and slag formation are usually increased (0.6-0.9 ton per ton of iron).

Bessemer pig iron (also known as acid Bessemer iron) is intended for the production of steel in converters by the acid Bessemer process. It bears close resemblance to low-silicon foundry iron both in chemical analysis (see Table 5) and in smelting conditions. Phosphorus must be not over 0.07 per cent. Therefore, the ore for acid Bessemer iron should be free from phosphorus.

Open-hearth pig iron (Table 5) is converted into steel in open-hearth furnaces. Silicon should preferably run between 0.6 and 0.9 per cent. As much as 0.3 per cent phosphorus will not affect steel quality. Sulphur should be kept under 0.06 per cent. The coke ratio for open-hearth pig iron usually is 0.75 to 0.9 ton per ton of iron.

Thomas pig iron (also known as basic Bessemer iron) is converted into steel in converters by the basic Bessemer process. It is relatively high in phosphorus (1.5-2 per cent) and low in silicon (about

Table 5

**Analyses of Conversion or Steelmaking (Open-hearth, Acid Bessemer
and Basic Bessemer) Pig Irons**
(per cent)

Grade	Silicon	Manganese			Phosphorus			Sulphur		
		Iron group			Iron class			Iron category		
		I	II	III	A	B	C	I	II, max.	III
M1	0.91-1.5	1.5-2.5	2.51-3.5 3.51 & more		0.15	0.2	0.3	0.03	0.05	0.07
M2	0.3-0.9	1.5-2.5								
B1	0.9-1.6	0.6-1.2	—	—	0.07	—	—	—	0.04	—
B2	1.6-2.0	0.6-1.5								
T1	0.2-0.6	0.8-1.3	—	—	1.6-2.1	—	—	—	—	0.08

Note: The letters in grade designations stand as follows: "M" for open-hearth; "B" for (acid) Bessemer; and "T" for Thomas (basic Bessemer).

0.5 per cent). At a high rate of furnace operation, cold low-silicon irons are produced.

Special irons (Table 6) include ferrosilicon (10-12 per cent Si), spiegeleisen or spiegel (12-20 per cent Mn), and ferromanganese (60-80 per cent Mn). They differ in carbon content, high-silicon grades carrying less than 3 per cent. In grades containing 80 per cent Mn, the carbon content is not less than 7 per cent. These irons are produced at high temperatures of running, increased coke ratios (2-2.5 tons of coke per ton of iron), and a blast temperature of 750 to 900°C.

Slags. The slag flushed from a blast furnace consists essentially of three oxides: 30 to 40 (sometimes 45) per cent silica (SiO_2), 10 to 20 (sometimes 25) per cent alumina (Al_2O_3) and 40 to 50 per cent calcium oxide (CaO).

For efficient furnace operation, it is essential that the slag be sufficiently fluid at about 1450°C. A dense and viscous slag ham-

pers normal furnace working. It sticks to the bosh lining to form what is known as scaffolds, interferes with the descent of the burden, and is difficult to flush from the furnace.

Blast-furnace Ferroalloys
(Special Irons)

Table 6

Grade	Composition, per cent			
	Silicon	Manganese	Phosphorus	Sulphur
<i>Blast-furnace ferrosilicon</i>				
ΦC1	13.1	} 3.0	0.15	0.04
	and more			
ΦC2	9.0-13.0			
<i>Blast-furnace ferromanganese</i>				
MH5	2.0	75.1	0.35-0.45	} 0.03
MH6	2.0	70-75	—	
<i>Blast-furnace spiegel and silicospiegel</i>				
31	—	20.1-25.0	0.22	} 0.03
32	2.0	15.1-20.0	0.20	
33	—	10.0-15.0	0.18	
CMH1	9.0-13.0	18.0-24.0	0.20	

The fusibility or the viscosity of blast-furnace slags is a function of its lime, silica and alumina contents. A slag will be sufficiently fluid when the ratio of ($\text{SiO}_2 + \text{Al}_2\text{O}_3$) to CaO is close to unity. The viscosity of slags at 1500°C ranges between 2 and 5 poises.

The Blast-furnace Gas. As formed in the hearth zone, the blast-furnace gas contains approximately 35 per cent CO , 64.2 per cent N_2 and 0.8 per cent H_2 at a blast humidity of about 1 per cent. As it passes upward, the composition of the gas changes.

Above the tuyeres, where direct reduction reactions mainly take place, the gas picks up carbon monoxide. Higher up the stack, some of the carbon monoxide effects indirect reduction, forming carbon dioxide without any change in the total volume of the gas. The gas is further enriched with carbon dioxide due to the decomposition of the limestone. In the high-temperature zone, the water of hydration from the larger lumps reacts with the carbon monoxide and carbon to form carbon dioxide, carbon monoxide and hydrogen.

The blast-furnace gas is burned in hot-blast stoves, boilers, etc. Its average composition (for a coke-fuelled blast furnace) is 8-12 per cent CO_2 ; 39-40 per cent $\text{CO} + \text{CO}_2$; 0.2-0.4 per cent CH_4 ; 2.5-3 per cent H_2 ; and 57-58 per cent N_2 .

21. Blast Furnace Working

Furnace working mainly depends on its temperature and on the rate and uniformity of burden descent.

Watch on furnace working is provided by blast-furnace instruments. They measure and record blast temperature and pressure, top gas temperature and pressure (separately for each gas off-take), and lining temperature at several points up the furnace. The level of the stockline is determined by two automatic prods whose readings are recorded on charts. On the more recent designs, this job is done more accurately by ultrasonic prods. At regular intervals, samples of top gas are taken for analysis.

The dust catchers are cleaned and the collected flue dust is weighed every two hours or often. The information thus obtained helps to readjust the composition of the burden so as to maintain the driving of the furnace normal.

With control of the blast furnace becoming more a science than an art, such irregularities in its working as chilled hearths, burden slips, flaring, scaffolding, hanging, etc., are becoming increasingly more seldom.

Yet, control of the furnace by a human operator who readjusts its run on the strength of instrument readings can no longer keep pace with modern requirements. Nor is automatic control of some variables (say, the blast) sufficient. Therefore, recent automatic control systems have been designed to continuously monitor the quality and quantity of the materials fed and produced in the blast furnace and to adjust the temperature and pressures accordingly.

The following process variables constitute the basis of a typical blast-furnace control system:

(1) Pig iron produced for 1000 normal cu m of blast introduced in the furnace. This variable is a function of the heat balance, furnace output and rate of driving.

(2) Carbon consumption per ton of pig iron. This is the principal variable of the heat balance and an index of furnace efficiency.

(3) Minute furnace output, as a measure of the driving rate.

(4) Minute carbon consumption, as a measure of the thermal condition of the furnace.

(5) The size and composition of the burden.

(6) Carbon burned with the oxygen of the burden and blast.

(7) The composition and temperature of the top gas.

The deviation of any of the variables from a prescribed value is automatically sensed by the respective instruments. The variables are related with one another by equations which are solved by a computer, and the latter produces the necessary corrective pulses driving the final control elements or actuators.

Almost all operations in blast-furnace shops are mechanised and automated now. Therefore, a shop of four furnaces with a total daily output of about 6500 tons of iron will be run by a staff of about 400.

22. Efficiency of the Blast Furnace

The efficiency of a blast furnace is mainly assessed on the basis of its daily output and coke ratio (coke per ton of pig iron). A basis for comparing the efficiency of different blast furnaces is provided by the utilisation factor which is the ratio of the useful volume to daily output of a furnace, or:

$$K = \frac{V}{P} \text{ cu m per ton per day}$$

The utilisation factor for blast furnaces producing steel-making iron ranges between 0.7 and 0.85 cu m/t. At the leading Soviet iron works it is 0.58 cu m/t.

The coke ratio gives an idea about the economic efficiency of a furnace. With further progress in furnace control and burden preparation, it has been continually reduced. At present, the coke ratio is 0.6 to 0.8 ton per ton of pig iron.

The run of a furnace (or its cast time) is assessed in terms of the stay of a given burden in the furnace. As a rule, it is 6 or 7 hours.

The overhaul period, i.e., the period between the blowing-in of a furnace and its blowing-down for major repairs, varies with the quality of refractories, furnace design, and the operator's skill. Usually, it is 4 or 5 years. Some furnaces are known to have been in operation for 10 to 11 years running.

One of the methods improving the output and efficiency of blast furnaces is to operate it under a high top pressure. Another method is to remove the sulphur from the pig iron outside the furnace, by adding desulphurising agents into the spout when the iron is being tapped or into a ladle car. This method makes it possible to use slags of higher acidity and, consequently, to reduce coke consumption.

Still another method is the removal of the silicon from the pig iron while it is in a ladle car by blowing it over or through with air enriched with pure or commercial oxygen. This method appreciably reduces the content of the impurities, thereby simplifying blast-furnace production and conversion of pig iron into steel.

The use of a blast with oxygen enrichment up to 23-25 per cent results in the higher temperatures of the hearth and top gas, increased carbon monoxide concentration in the blast-furnace gas, more efficient reduction, better furnace efficiency and output.

Oxygen enrichment to a higher percentage is advantageously used in the blast-furnace smelting of ferrosilicon and ferromanganese.

The use of a moistened blast expands the combustion zone, which fact improves furnace operation. In the case of a moistened blast, it has to be heated to a higher temperature in order to make up for the heat spent to decompose the water.

Chapter V

THE MANUFACTURE OF STEEL

A. THE BESSEMER PROCESSES

23. The Acid Bessemer Process

By this process, the carbon, silicon and manganese of molten iron can only be eliminated by blowing a current of air through the metal, converting it into steel. The process is also known as the fuelless, as the metal and slag are melted due to the heat liberated by the oxidation of carbon and silicon.

The vessel in which pig iron is converted into steel by the Bessemer process is known as a converter. It consists of a steelplate shell lined with silica bricks. For this reason, acid slags are formed, and hence the name—the acid Bessemer process. The acid process will not eliminate phosphorus or sulphur from the metal.

The charge for the converter, which must be molten, is brought in hot-metal ladle cars. In charging, the converter is tilted into a horizontal position (Fig. 50), and the hot metal is poured into its nose. The blast is put on (under a pressure of 2 to 2.5 atm gauge), the vessel turned upright, and the heat blown. The blast is introduced through the tuyeres in the bottom. The time of blowing is 10 to 18 minutes, depending on the content of the impurities. The thorough mixing of the constituents of the charge and the generation of much heat by oxidation make the Bessemer process a rapid one. The molten steel is poured into a ladle car, and the slag into a slag pit. The daily production of a converter 25 to 30 tons per heat in size is 1200 tons, which is enough to cater for the output of a big blast furnace.

Oxidation in the Bessemer Process. The possibility and sequence of oxidation in a Bessemer converter depends on changes in the free energy, ΔG , of the reactions $2M + O_2 = 2MO$. Since $\Delta G = -RT \ln K_p \approx -RT \ln \frac{1}{p_{O_2}}$, whether or not an oxidation reaction is possible can be judged from the dissociation pressures of oxides (p_{O_2}) (Fig. 51).

The greater the free energy change, ΔG , of oxide formation, the greater is the affinity of a given element for oxygen and the easier, other conditions being equal, it is oxidised.

Up to 1750°K, the sequence of elements in their affinity for oxygen is as follows: calcium, magnesium, aluminium, silicon, manganese, chromium, iron, nickel, copper.

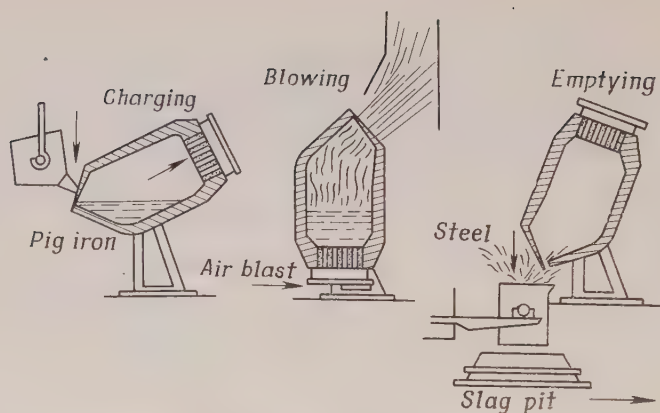


Fig. 50. The stages of the Bessemer process

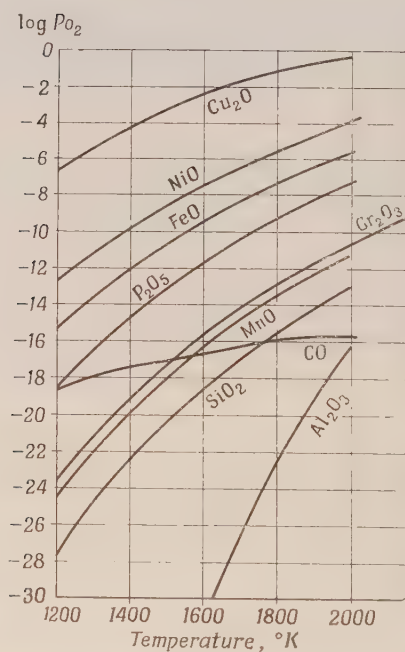


Fig. 51. Dissociation pressure of some oxides related to temperature

As the temperature increases, the affinity of metals for oxygen decreases non-uniformly, and their sequence may be changed. For example, at 1300°K the sequence in which the elements are oxidised is as follows: silicon, manganese, chromium, carbon, and iron. At 1750°K, silicon is followed by carbon, manganese, chromium, and iron. At 1900°K, carbon oxidises first and is followed by silicon, manganese, chromium, and iron.

The fact that in pig iron the impurities are in solution, their affinity for oxygen is also affected by their concentration (activity) in the iron. Below saturation the activity is less than unity and will further decrease with decreasing concentration, and the element will be more difficult to oxidise.

When the pig iron in a converter is blown with air, the oxygen of the blast more often runs into the atoms of irons some of which are oxidised:



The ferrous oxide mixes with the metal and partly dissolves in it; at the same time the ferrous oxide reacts with the impurities. Having a greater affinity for oxygen than iron, the impurities are readily oxidised by the ferrous oxide and less by the oxygen of the blast.

The Charge. The charge for the acid Bessemer process consists of molten pig iron, scrap, and rich iron ore.

As the acid process cannot eliminate the sulphur and phosphorus content of the metal, the relevant U.S.S.R. Standard stipulates that acid Bessemer pig iron shall contain not more than 0.07 per cent phosphorus and 0.06 per cent sulphur.

The silicon and manganese content of the pig iron should be sufficient to generate enough heat. Normally, the respective contents are 1.2-1.5 per cent Si and about 1 per cent Mn.

The carbon content of acid Bessemer iron usually ranges between 3.8 and 4.2 per cent.

The process starts at the temperature of the molten iron poured into the converter, i.e., at 1250 to 1350°C.

For higher efficiency, better control and steady results, it is important to equalise irregularities in the composition of the different blast-furnace casts for the Bessemer heats. This purpose is served by mixers (Fig. 52).

Conversion of Iron to Steel. Three clearly distinctive stages may be noted in the conversion of normal pig iron into steel by the acid Bessemer process (Fig. 53).

The first stage commences as soon as the blast is put on. The oxygen of the blast oxidises the iron to ferrous oxide. As a slag, the ferrous oxide mixes with the metal. Having a greater affinity

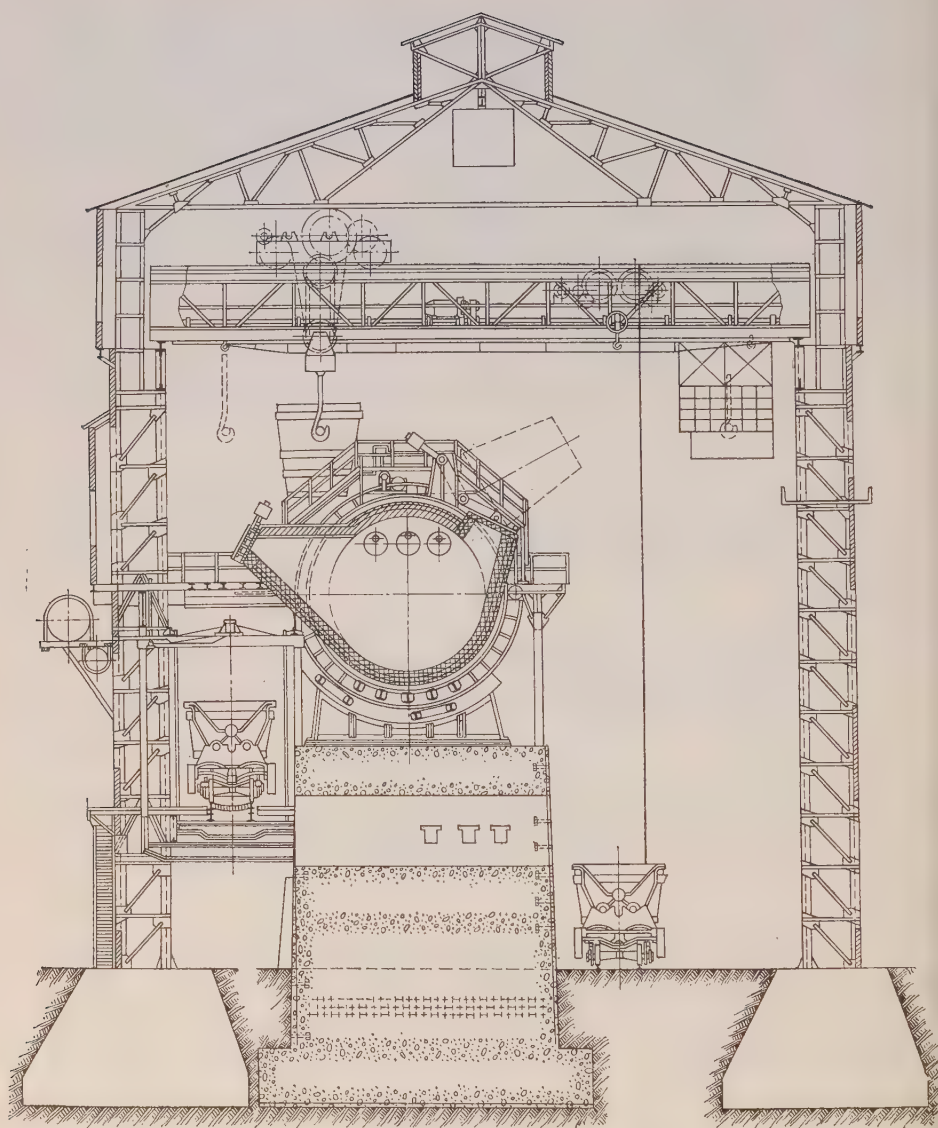
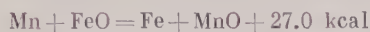


Fig. 52. Section through a mixer and mixer-house

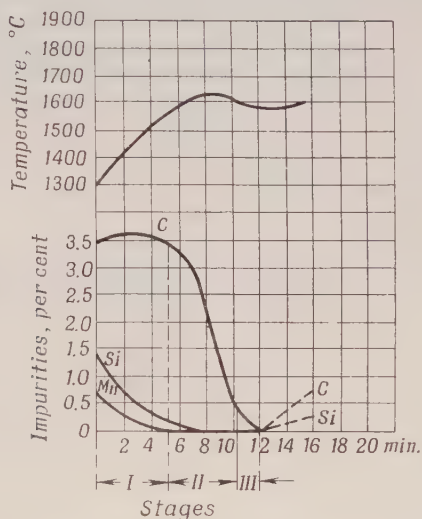
for oxygen, the silicon and manganese rob the iron of its oxygen according to the following reactions:



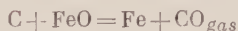
and separate as oxides (insoluble in the molten metal) into the slag. This stage lasts for three or four minutes, and may be called the slag formation period.

The second stage commences after the oxidation of iron, silicon and manganese, when the metal bath has reached a temperature

Fig. 53. Progress of the acid Bessemer blow



of 1600 to 1625°C, and the dissolved carbon is oxidised by the ferrous oxide of the slag according to the reaction



The gas evolved during this stage is rich in carbon monoxide which burns at the nose of the converter with a dazzling white flame 5 or 6 m high. The oxidation of the carbon during the second stage proceeds with high intensity, and the blast cannot supply enough oxygen any longer. For this reason, the carbon deoxidises the iron oxides in the slag. This reaction is endothermic; besides some heat is lost with the gas and through radiation; and so the temperature of the molten bath is reduced towards the end of the second stage.

The third stage begins when the flame "drops"—a sign that the carbon has been practically removed from the charge. Instead

the oxidation of the remaining silicon and manganese and then of some iron is stepped up.

Owing to high temperature, some iron, manganese and their oxides are evaporated. Their vapours are oxidised to Fe_3O_4 and Mn_3O_4 at the nose and impart a brown colour to the gas. The third stage lasts for 1 to 3 minutes.

In Soviet practice, the blow is continued until all the impurities have been eliminated, and the metal is cast after the necessary finishing and alloy additions are made.

Where carbon steel is the final product, the blow is discontinued after the desired carbon content has been attained, in which case there is no third stage in the process.

The quantity of slag formed is about 5 to 7 per cent of the metal made and approximates the following range of composition: SiO_2 , 53-55 per cent; Al_2O_3 , 0.5-1.0 per cent; MnO , 18-22 per cent; and FeO , 20-25 per cent.

When the molten metal is high in silicon and manganese, the heat produced by their oxidation may be excessive and cause the metal to blow too hot. As a result, the carbon will be eliminated before the impurities, and there will be an excess of silicon and manganese in the metal towards the beginning of the third stage. Then, in addition to difficulties in obtaining the desired analysis, the metal will be overcharged with dissolved gases. The remedy against too high a temperature of the blow is to add some scrap which will bring down both the carbon burn-out and the content of silicon and manganese.

When the molten metal is low in manganese and silicon, the metal is liable to blow too cold, owing to insufficient heat being produced by the oxidation of the impurities, and the process will be delayed. The temperature of the heat may be then raised by adding some ferrosilicon or spiegeleisen.

24. The Basic Bessemer (Thomas-Gilchrist) Process

As distinct from the acid Bessemer process, its basic variety removes phosphorus and to some extent sulphur.

The basic process was adapted to Bessemer working in 1878 by Thomas and Gilchrist. In basic Bessemer practice the vessel is the same as that used for acid working, except for lining of dolomite. The dolomite bottom is rammed in place with a tar binder with an addition of clay. Both the dolomite lining and rammed bottom are fired to above the temperatures of possible transformations in the refractory materials. Owing to the basic lining, basic slags may be used, high in lime. In such a case, after the silicon, manganese and carbon have been oxidised, phosphorus removal is effected

during the blow by oxidation to the pentoxide (P_2O_5) and subsequent formation of calcium phosphate ($4CaO \cdot P_2O_5$) which becomes a constituent of the slag.

The Charge. The charge for the basic Bessemer process consists of molten pig iron, scrap, lime and iron ore.

The necessary heat is supplied during the blow by the oxidation of phosphorus. Normal basic Bessemer pig iron (see Table 5) contains 1.8-2 per cent P. Silicon is a detrimental impurity, as the silica obtained by its oxidation adds to the quantity of slag, scours the lining, and requires additional lime to flux it. For this reason, silicon must be kept to below 0.5 per cent. Manganese prevents excessive oxidation of the iron and makes the slag more fusible.

Basic Bessemer pig iron is produced in a blast furnace with low temperatures of running; for this reason, it is relatively high in sulphur.

When poured into a basic converter, the pig iron is raised to $1180-1250^{\circ}C$. Yet, it can be easily blown as the phosphorus makes it fluid in the molten state. Before a charge of pig iron is poured, the converter is loaded with 15 per cent lime of the metal weight to be charged. The limestone should be calcined on the spot, as during prolonged storage and in transit it easily absorbs the moisture and carbon dioxide of the air. The other constituents of the charge should meet the same requirements as their counterparts in the acid process do.

Conversion of Pig Iron to Steel by the Basic Process. The blow can again be divided into three stages (Fig. 54).

During the first stage the iron, silicon and manganese are oxidised. The molten metal is heated slowly due to the low silicon content of the charge. The slag of the first stage consists of oxides of iron, silicon and manganese.

During the second stage the carbon is oxidised. Though during the first stage the temperature is low and the bath is cold, the carbon is oxidised readily, due to the high fluidity of phosphorus irons and the increased content of iron oxide in the slag. As in the acid process, the second stage can be easily identified by the flame at the nose of the vessel. The flame, however, is never white, as the temperature of the heat in basic working is lower than in acid working.

During the second stage the slag changes in composition, as it picks up more lime. Towards the end of the second stage the temperature of the molten metal drops, as the oxidation of carbon in the slag by ferrous oxide absorbs much heat; the flame flickers and drops, because practically all carbon is now burned.

During the third stage, the phosphorus is vigorously oxidised by the ferrous oxide contained in the slag. The oxidation of the

manganese, silicon and carbon during the first and second stages helps the subsequent oxidation of the phosphorus in that the pentoxide cannot now be reduced by any one of them. By the moment the third stage begins, the lime has been fully dissolved in the slag, and the P_2O_5 unites with such lime to form the stable

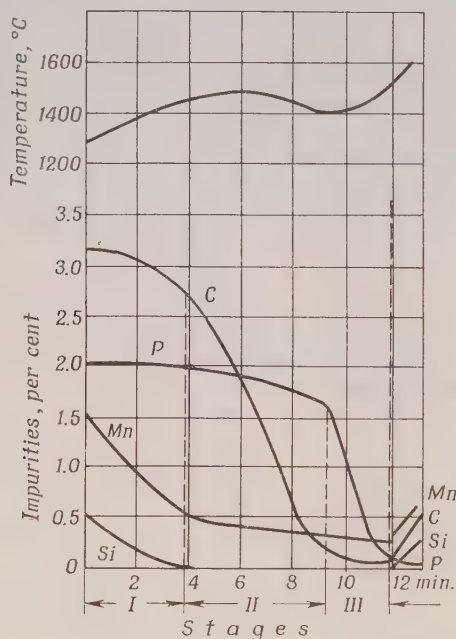
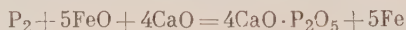


Fig. 54. Progress of the basic Bessemer blow

phosphate $4CaO \cdot P_2O_5$ which in turn is absorbed by the slag. Both reactions may be presented as follows:



and they are accompanied by the evolution of much heat (about 350 kcal). This is the reason why the oxidation of the phosphorus raises the temperature of the bath (see Fig. 54). This oxidation, however, slows down as phosphorus concentration decreases. As a result, increasingly more iron is oxidised towards the end of the blow. A sign of this condition is the brown fumes at the nose of the vessel. The blow is discontinued after the phosphorus content has been reduced to 0.05-0.08 per cent. Complete phosphorus removal is unattainable, as it involves increased iron losses.

The slag produced by basic working consists of calcium silicates $nCaO \cdot SiO_2$, calcium aluminates and ferrites $CaO \cdot Al_2O_3$ and $CaO \cdot Fe_2O_3$, calcium phosphates $3CaO \cdot P_2O_5$ and $4CaO \cdot P_2O_5$. Because

of their high content in phosphoric acid, basic Bessemer slags have value as a fertiliser.

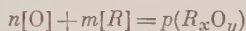
The slag weight is 18 to 20 per cent of the metal made. Its percentage composition is SiO_2 , 3-5 per cent; P_2O_5 , 15-25 per cent; Al_2O_3 , 0.5-1.0 per cent; CaO , 48-52 per cent; MnO , 5-7 per cent; and FeO , 12-15 per cent.

25. Finishing Additions

If the heat from a converter were poured in that condition after the blow is cut off, the resultant steel would be unsuitable for rolling and forging due to red and cold shortness caused by the dissolved oxygen.

This condition is remedied by adding some agents which rob the iron of its oxygen while teeming the steel into the pouring ladle; these agents are called deoxidisers.

Deoxidisers react with the dissolved oxygen according to the reaction:

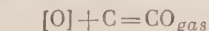


For efficient deoxidation, it is essential that the oxide formed by a deoxidiser be nearly insoluble in iron and would separate from it by floating.

For the deoxidation reaction, the equilibrium constant is $K \approx \frac{1}{[\text{O}]^n [\text{R}]^m}$. Therefore, $[\text{O}]^n \approx \frac{1}{K [\text{R}]^m}$. In other words, the quantity of oxygen dissolved in the metal decreases with increasing concentration of the deoxidiser in the molten metal.

The deoxidising ability of elements increases directly with their affinity for oxygen which in turn grows stronger with an increase in the change of the free energy of reaction.

Aluminium is the most powerful deoxidiser. The deoxidisers that are most commonly used in steel making are carbon (as charcoal, coke breeze or as a constituent of spiegeleisen and ferroalloys), manganese (as ferromanganese), silicon (as ferrosilicon), and aluminium (in metallic form or in alloys with manganese and silicon). Deoxidation reactions may be presented as follows:



In deoxidation it is as important to remove the resultant oxides, or the metal will be contaminated by non-metallic inclusions. Oxide removal is facilitated by the fact that some of them (MnO , SiO_2) form with the dissolved oxygen MnO-FeO solutions, silicates of

ferrous and manganese oxides which have a much lower melting point than pure oxides.

The efficiency of deoxidation can be improved by using composite deoxidisers consisting of several elements.

Rimming steels are only slightly deoxidised in the converter. Final deoxidation is effected by their own carbon while they are cast into moulds.

Killed steels are completely deoxidised, usually by manganese and silicon thrown into the converter or ladle.

In basic Bessemer working, it is essential to flush the phosphoric slag before the additions are made to the converter, or the FeO content of the slag may be reduced too and the metal may pick up much phosphorus. After deoxidation the metal is poured.

26. Converter Construction

Bessemer vessels are built in sizes up to 80-100 tons capacity per heat. A cross section of the Bessemer vessel is shown in Fig. 55. It consists of a steel shell made up of three detachable sections—bottom, body, and hood or nose.

The only difference between an acid and a basic converter is that in the former the lining is of silica, and in the latter of dolomite. Furthermore, a basic converter has a thicker bottom (900-1100 mm) than an acid one (420-750 mm); and the volume per ton of steel made is greater in the former than in the latter.

Thomas converters have to have more space per ton of metal than Bessemer converters, since the oxidation reactions in the former are more violent and more slag is formed.

The body section is cylindrical and fits into a stout steel ring called the trunnion belt. The converter is supported by two trunnions carried by pedestal bearings so that the converter can be rotated about the trunnions.

One of the trunnions is hollow. A pipe leads from the hollow trunnion to the windbox at the bottom of the vessel and the blast can be kept on irrespective of the position of the converter. The converter is tilted by a toothed wheel attached to the other trunnion and is rotated by a rack actuated by an electric motor.

Fig. 56 shows a cross-section through a Bessemer shop. It consists of seven areas: (1) a mixer bay; (2) a converter bay; (3) a pouring bay; (4) a ladle-repair bay; (5) a bottom-making bay; (6) a stock bay; and (7) a refractory storage bay.

As a rule, a Bessemer shop has three or four converters. From the mixer the molten pig iron is carried in ladle cars. The steel is poured into a teeming ladle car which takes the metal to the pouring bay.

Each converter is served by a turboblower. For a converter of 30 to 40 tons capacity per heat, the blower should deliver 1500 cu m of air per minute at a pressure of 2.6 atm (gauge).

The body lining of an acid Bessemer converter lasts for 1000 to 3000 heats. The bottom is worn away in 20 to 30 blows. The

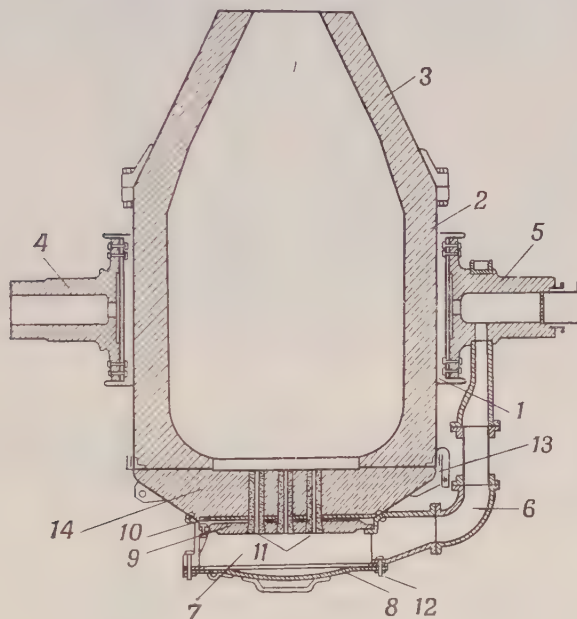


Fig. 55. Vertical section of a Bessemer converter:

1—trunnion belt; 2—main shell or body; 3—hood or nose; 4—trunnion coupled to tilting mechanism; 5—hollow trunnion admitting blast; 6—elbow blast pipe connecting hollow trunnion with windbox (or air chest); 7—windbox (or air chest); 8—detachable cover of windbox; 9—tuyere cover; 10—bottom foundation; 11—tuyeres; 12—cover catcher (or cotter); 13—clamp holding together main shell and bottom section; 14—bottom section

respective figures for a basic Bessemer (Thomas) converter are 350-400 and 40-75. The consumption of air is about 300 cu m per ton of steel. The conversion losses account for 11 to 9 per cent of the pig iron charged.

The construction costs of a Bessemer plant are lower than those of an open-hearth plant.

27. Side-blown Converter Practice

This type of converter usually has a capacity of 1, 1.5, 2 or 2.5 tons per heat. The lining (Fig. 57) is of silica brick. The air is introduced through the side of the vessel, using a windbox and a series

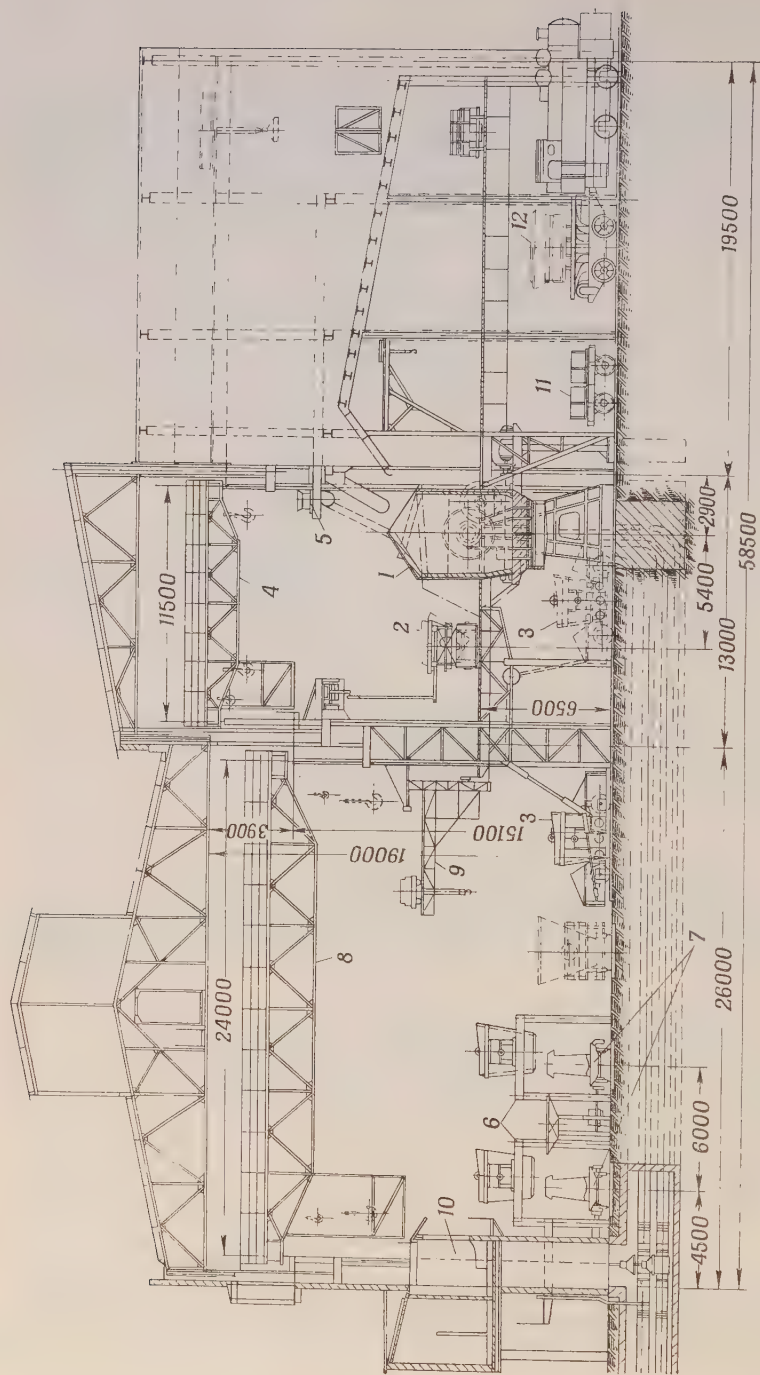


Fig. 56. Layout of a modern Bessemer shop:

1—converter; 2—hot-metal transfer ladle; 3—steel teeming ladle mounted on bogie; 4—overhead travelling crane in the converter bay; 5—beam-riding crane; 6—hoppers and chute; 7—pouring platform; 8—slag ladle car; 9—control platform; 10—overhead travelling crane in the pouring bay; 11—bottom-changing bogie; 12—overhead travelling crane.

of tuyeres. The brickwork near the tuyeres is built up to compensate for heavy scouring.

The air is blown under a pressure of 200 to 300 mm Hg. The charge is poured through the nose of the tilted vessel. When the blow is put on, the vessel is tilted through an angle of 10 to 15°. By allowing the tuyeres to deliver free air above the surface of the metallic bath, some iron is oxidised to ferrous oxide which in turn oxidises the silicon, manganese and some of the carbon.

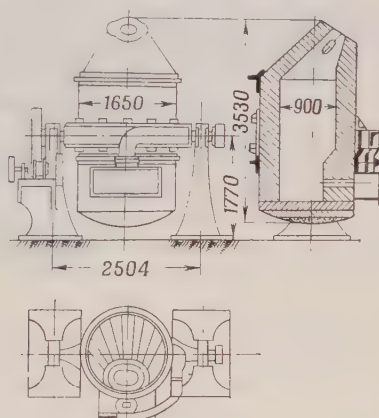


Fig. 57. Side-blown converter of 1.75-ton capacity

The oxidation of the silicon and manganese raises the temperature of the bath, and the carbon begins to form carbon monoxide. The carbon monoxide burns above the molten metal, raising its temperature still more and stepping up the oxidation of the carbon. The bath begins to boil, and the tuyeres are allowed to blow the air through the body of the charge. In a few minutes, the metal settles down—a sign that practically all carbon has been burned, and the tuyeres are again controlled to deliver free air above the surface of the metal to burn such carbon monoxide as may be still evolved. The bath absorbs the heat, and the metal blows hotter than in large Bessemer vessels. The metal obtained in side-blown converters casts well, for which reason the process is chiefly used in the foundry shops of engineering works.

28. Oxygen Steelmaking

Steelmakers have long been interested in a process which could combine the high-quality product of the open hearth with the greater production rate of Bessemer converters. As a result, a variety of oxygen steel-making processes have appeared.

A relatively recent addition to oxygen steel-making technology is the Linz-Donawitz process. In this process, termed the LD process for short, the conversion of pig iron is effected in vessels with no opening in the bottom, lined with dolomite or magnesite on a tar binder. A blast of almost pure oxygen is blown vertically by a water-cooled lance. The tip of the lance is within about 1200 mm of the surface of the bath (Fig. 58).

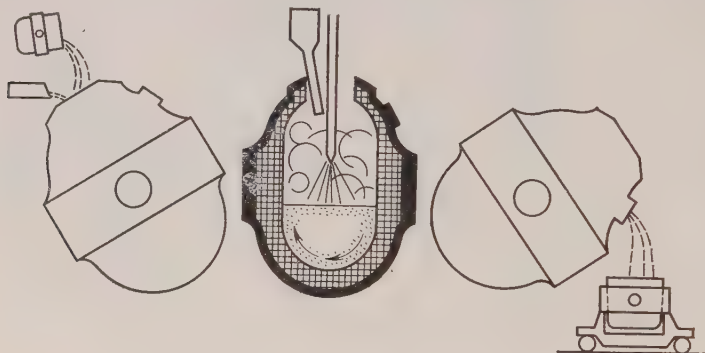


Fig. 58. The stages of the LD process

Phosphorus removal and carbon oxidation proceed practically simultaneously. For this reason, when the blow is stopped at the desired carbon content, the phosphorus concentration is sufficiently low (0.015 per cent). Sulphur removal is very efficient, and its content in LD steels is often lower than in open-hearth grades. Nitrogen concentration in LD steels is likewise lower than in open-hearth grades for the reason that the metal is prevented from absorbing nitrogen by the intensive evolution of carbon monoxide and the oxygen blast delivered onto the surface of the metal. The LD process runs hot. The charge, in addition to molten pig iron, includes some scrap and iron ore. Lime is added during the blow. Blowing time is 18 to 20 minutes. The oxygen consumption is above what is theoretically necessary for the oxidation of the impurities. The use of commercially pure oxygen supplies ample heat, and pig iron of practically any analysis can be worked. Scrap consumption varies from iron to iron and may sometimes reach 30 per cent.

The flexibility of the LD process is amazing. The blow can be stopped at any desired carbon content, especially when the pig iron used is of the low- or medium-phosphorus quality. The converted steel may be of widely varying grades, both plain carbon and alloy, such as rail steel, ball-bearing (C-Cr) steel, shafting

(Cr-Mo) steel, spring (Si-Mn) steel, etc. These advantages have won the LD process general recognition. It is expected that over 20 million tons of steel will be produced by this process annually in the near future. The capacity of LD converters is steadily increasing, the most commonly used size being 100 tons per heat. Plans are afoot to build 225-ton and 270-ton vessels.

Steelmakers in Belgium and Luxemburg are successfully using the LD-AC process for the conversion of phosphorus pig iron. In this process, which is a modification of the LD process, two or more slags are used at a time, the slag of the previous heat being left in the vessel. The phosphorus is efficiently removed by charging finely divided lime with the oxygen through the oxygen lance.

Another basic oxygen steel-making process is the Kaldo process. In the Kaldo process, the furnace is inclined and rotates on its axis. The oxygen stream blown through the lance in the nose does not penetrate the bath surface as in the LD process but is directed at a low angle over the top of the molten metal. The rotation of the vessel speeds up reactions between the metal and the slag. The semiclosed shape of the vessel and the oxygen blast serve to burn the CO to CO₂ so that the full calorific value of each unit of carbon is utilised within the body of the furnace, and the temperature of the bath is raised thereby. With the oxygen blast blown at a lower pressure (3 atm) than in the normal basic oxygen process, the process is quiet and less iron is lost with flue gases. On the other hand, blowing time is twice as great as in the LD process.

Some of the Kaldo vessels currently in service are as large as 110 tons per heat. However, the process as a whole is less common compared with the LD process due to the complexity of rotating vessels.

Another type of oxygen steel-making process also using a rotating vessel is the Rotor process. A Rotor vessel uses two oxygen lances. One of them is submerged in the molten metal, and the other is allowed to deliver oxygen over the surface of the bath. The primary oxygen purifies and stirs the metal, while the secondary oxygen burns what CO may appear above the bath. The run of the heat is controlled by varying the flow rate of primary and secondary oxygen. Rotor vessels are built in sizes of 100 to 110 tons capacity per heat.

29. Uses for Converter Steel

The main drawback of steel produced in any type of converter is the increased content of gases, especially nitrogen which may run 0.01 to 0.03 per cent against 0.003 to 0.008 per cent in open-hearth steel.

Basic Bessemer (Thomas) steel contains more oxygen, nitrogen and slag inclusions than does acid Bessemer steel. For the same reason, the former is of a lower quality than the latter.

Converter steels have limited uses. Quality, and less so high-quality carbon and alloy steels are not manufactured by any of the Bessemer processes. Much better steels are produced where the blast is enriched with or consists entirely of oxygen. In fact, their quality is very near to that of open-hearth steels. Among the factors contributing to this are the reduced partial pressure of nitrogen because of the presence of oxygen; the reduced pick-up of nitrogen by the molten metal; and reduced heat losses otherwise carried off by nitrogen. In addition to this, oxygen enrichment raises the oxidising nature of the blast and, what is especially important, makes it possible to convert low-silicon, low-manganese pig irons and melt much scrap.

High temperatures of converter running are in turn advantageous in that basic slags may be used with which more phosphorus and sulphur can be removed. For this reason, oxygen enrichment has become a major trend in modern steelmaking by converter processes.

B. THE OPEN-HEARTH PROCESSES

30. Principles of the Processes

In 1865, after many attempts Pierre Martin of France smelted steel in a gas-fired regenerative furnace developed by William Siemens in 1862 in which much higher temperatures can be obtained than in any furnace not using combustion by regeneration. In Europe this process is still known as the Siemens-Martin process.

Regeneration consists in the utilisation of waste heat for preheating the air and gaseous fuel before they are admitted into the furnace. In this way, some of the waste heat is returned to the furnace, and the temperature at which fuel burns is raised appreciably.

The gaseous fuel and air are preheated in heat-storing or "regenerator" chambers containing a honeycomb of checker bricks. A present-day open-hearth furnace fired with producer gas or with a mixture of blast-furnace and coke-oven gases has four regenerator chambers, two at each end of the furnace (Fig. 59). The waste gases are led by flues into one pair of the regenerator chambers to give up their heat to the checker brickwork and to be then discharged into the atmosphere through the stack. In the meantime, the gas and air for combustion are led into the other pair of regenerator chambers in which the checker brickwork has already been heated by the waste gases. After the first pair has grown sufficiently

hot and the other cold, the flow of the combustion gases and waste gases is reversed.

The fuel burning in the furnace with an excess of oxygen produces an oxidising atmosphere. The excess of oxygen and the carbon dioxide of the furnace gases oxidise the metal and its impurities

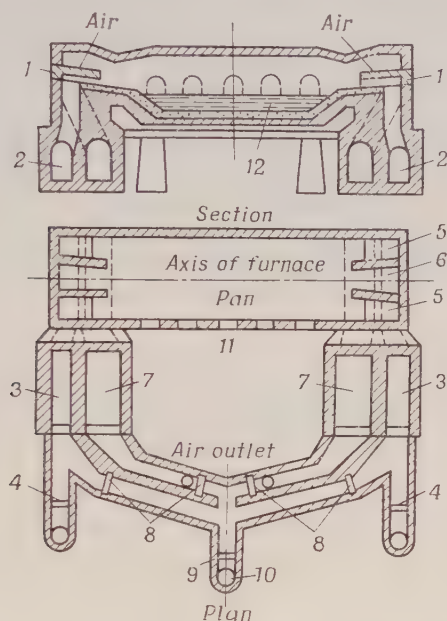


Fig. 59. Diagram of a gas-fired open-hearth furnace:

1—producer-gas ports; 2—slag pockets; 3—gas checkerwork; 4—gas inlet valve; 5—air uptake; 6—gas uptake; 7—air checkerwork; 8—flue-gas reversing valve; 9—flue-gas damper; 10—stack; 11—charging doors; 12—hearth

to form ferrous slags. Iron oxides oxidise the impurities of the pig iron. To speed up oxidation, some iron ore is thrown into the furnace. After the impurities of the charge are oxidised and eliminated as gas or slag, alloying additions and deoxidisers are introduced to obtain a high-quality steel of the desired chemical analysis, carrying very little nitrogen and slag inclusions.

The adaptability of the open-hearth process to prevailing local conditions, coupled with the high quality of the steel made, has stimulated its propagation. At the present time, about 85 per cent of all steel is produced in open-hearth furnaces.

31. The Open-hearth Furnace

Open-hearth furnaces have been built in capacities of 2 to 700 tons per charge, but the most common types at present are of 250 to 500 tons per charge.

In early open-hearth furnaces the refractory lining of the hearth, walls and arched roof was of silica brick. Over it in the hearth successive layers of quartz sand were sintered into a continuous bottom. For this reason, the slags were acid and the process was termed the acid open-hearth process. In 1880 a furnace was built in Russia in which the hearth and walls were lined with dolomite brick, and basic slags could be used. The process was named the basic open-hearth process. The basic process has proved more versatile and, therefore, is now dominating the field.

Except for the lining, both acid and basic open-hearth furnaces are fundamentally similar in construction. Fig. 60 shows a cross-section and a plan of a modern basic open-hearth furnace.

Charging is done through doors at one side of the furnace, and the metal is tapped through a tapping hole at the opposite side to which the hearth bottom gently slopes. The walls and arched roof are secured by buckstays and tie rods, and the entire furnace is supported by reinforced-concrete columns.

Table 7

Approximate Design Features of Basic Open-hearth Furnaces

Feature	Gas-fired furnaces				Residue-oil-fired furnaces	
	Capacity in tons					
	500	250	180	100	125	70
Hearth area, sq m	97	74	70	45	52	36
Hearth length, m	16.4	14.2	14	11.5	12	10
Bath width, m	5.9	5.2	5	3.9	4.3	3.6
Bath depth, mm	1170	1000	850	830	880	700
Hearth thickness, mm	1185	1100	1155	1050	1000	900
Volume of slag pits, cu m:						
on air side	292	127	45	30	—	—
on gas side	161	124	32	21	—	—
Volume of checkerwork, cu m:						
on air side	224	181	162	110	—	—
on gas side	175	132	121	85	—	—

The furnace hearth is a shallow pan (Figs. 60 and 61). Length L and width E are measured at the level of the charging doors. The product of L and E is assumed to be the area of the furnace hearth (Table 7). The depth of the pan is measured from the bottom at its lowest point to the port slopes.

Until quite recently, the arched roof of open-hearth furnaces was made of silica brick and supported by water-cooled girders. Unfortunately, silica melts at 1710 C, and the temperature in a silica-brick-lined furnace may safely be raised to not higher than 1680 or 1700 C, which fact seriously limits the potentialities of such furnaces. For this reason recent practice has been to line the roofs of open-hearth furnaces with heat-resistant chrome-magnesite brick which may be heated to 1800°C. For higher strength, the chrome-magnesite roof is suspended by tie rods from transverse girders (see Fig. 82).

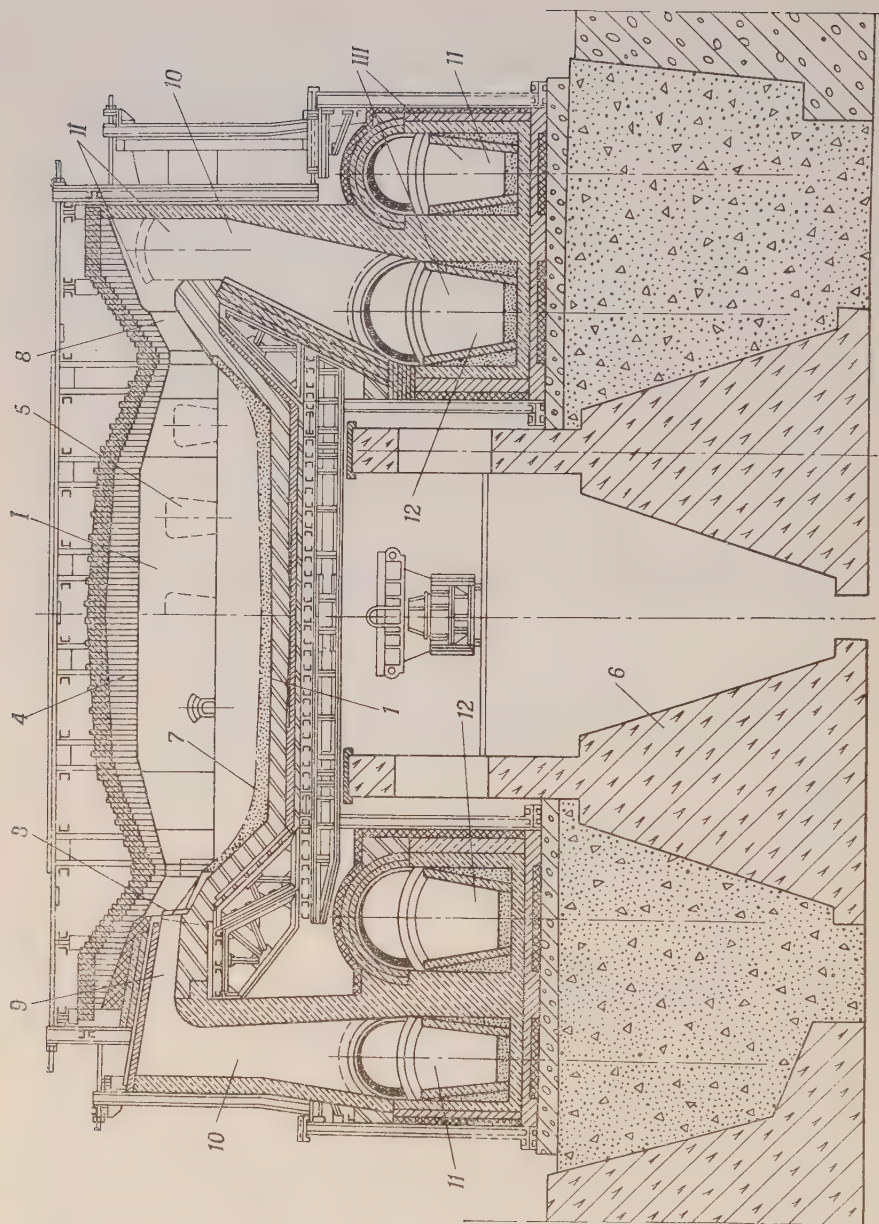
The silica roof lining usually gives an average life of 200 to 250 heats, the figure for basic roofs being 500 heats and more.

The gas is admitted into the furnace by a central uptake and air by two side uptakes. The uptakes terminate in gas and air ports respectively. The walls of the vertical flues around the ports are known as bulkheads (collectively, the walls and ports are also called the port block) which are subjected to much erosion. To extend their life and to shape the flame appropriately, some of their brickwork is usually replaced by a hollow steel box with water circulating inside it. On the outside the box is lined with firebrick. The remainder of the bulkheads and the walls of the uptakes are of silica brick, the more recent trend being to use magnesite, chrome-magnesite or forsterite brick for the purpose.

Where the furnace burns liquid fuel, there is no fuel port in the port block, and the fuel is injected by a burner projecting through the dog-house.

Any solid matter (dust and slag) carried over with the waste products settles on the bottom of the chambers placed before the regenerators and known as the *slag pockets* (Fig. 61). The use of chrome-magnesite brick in the vertical flues and slag pockets adds to their wear resistance and facilitates slag removal. In big open-hearth furnaces roll-out slag pockets are employed.

The *regenerators* (Fig. 61) are chambers filled with checker bricks which absorb and store heat, and divided by rider walls into several small flues which open into the larger flues. When the top courses of checker bricks are heated to 1250-1300 C in the air regenerator and to 1200 C in the gas regenerator, the valves are automatically operated to reverse the flow of air, fuel gas and waste products to and from either end of the furnace and regenerators.



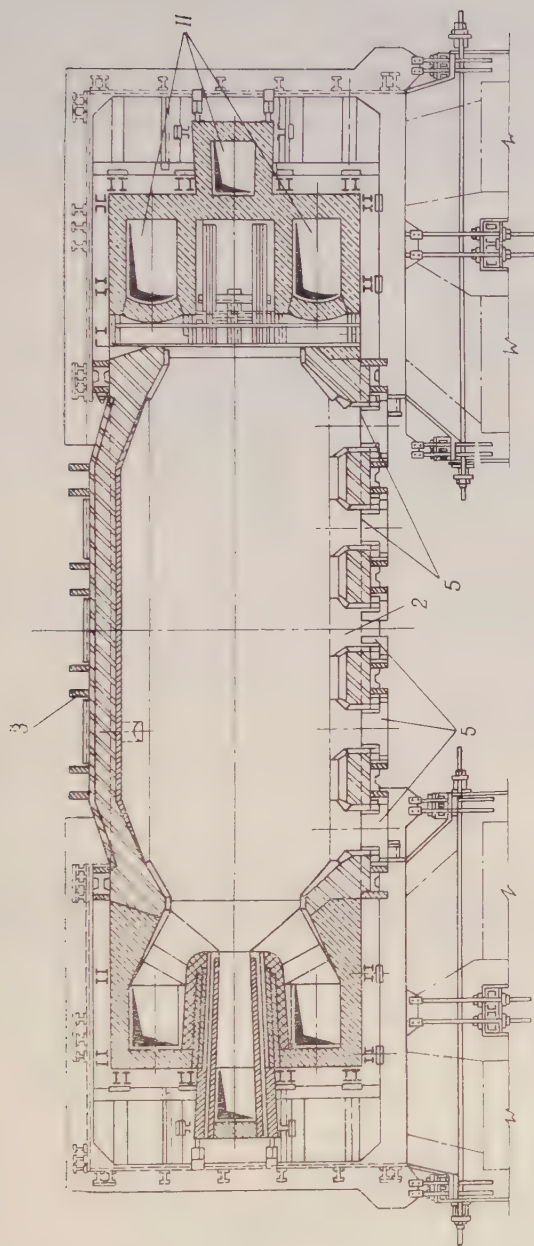


Fig. 60. Section and plan of regenerative furnace:

1—furnace space, 11—uptakes and bulkheads (port blocks); 111—slag pockets; 1—pan; 2—front wall; 3—end wall; 4—roof; 5—charging doors; 6—concrete supports; 7—port slope; 8—air port; 9—gas port; 10—vertical flues; 11—gas regenerator slag pocket; 12—air regenerator slag pocket

The *flues* to the stack and the power-operated *valves* are placed below the charging floor. On their way to the stack, the waste products pass through the slag pockets and regenerators to give up much of their heat to the checker bricks of the cooler regenerator. The incoming air and gas pass through the hot regenerator to absorb its stored-up heat. Forced draft is mainly employed in modern open-hearth furnaces.

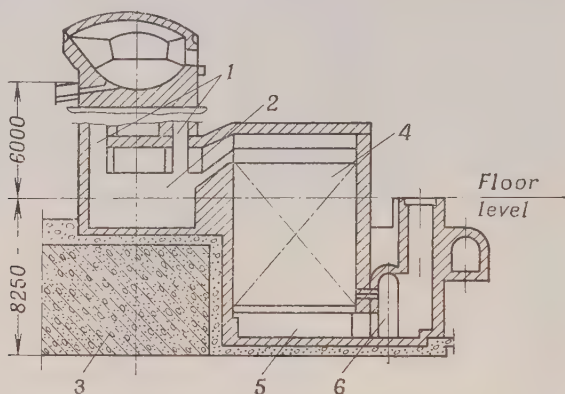


Fig. 61. Section through slag pocket and air regenerator:

1—air uptakes; 2—slag pocket; 3—slag pocket foundation; 4—checkerwork; 5, 6—checker flue

Open-hearth furnaces may be broadly classed into fixed or tilting. The latter are advantageous in the conversion of high-phosphorus pig iron. A tilting furnace is built into an iron shell carried by two segments and a row of rollers. Therefore, the furnace can be easily tilted to flush part or all of the slag, which has to be done more than once in the conversion of phosphorus pig iron.

In an open-hearth furnace plant (Fig. 62), the furnaces are arranged in a row. The plant is divided into areas, each performing its specific operation. The principal area is where the furnace (or furnaces) is located; it is charged and serviced from the charging floor on the charging side of the furnace building. The steel is run off on the tapping side into a steel ladle car. Also on the tapping side the steel is cast from the ladle into ingot moulds. Each area (stockyard, charging side, tapping side, mould-yard) has a crane of its own.

32. Open-hearth Fuels

Fuels for open-hearth furnaces must be of high calorific value and carry as little sulphur as practical.

Open-hearth furnaces may be fired with gaseous or liquid fuels. Among the former are blast-furnace, coke-oven or producer gas.

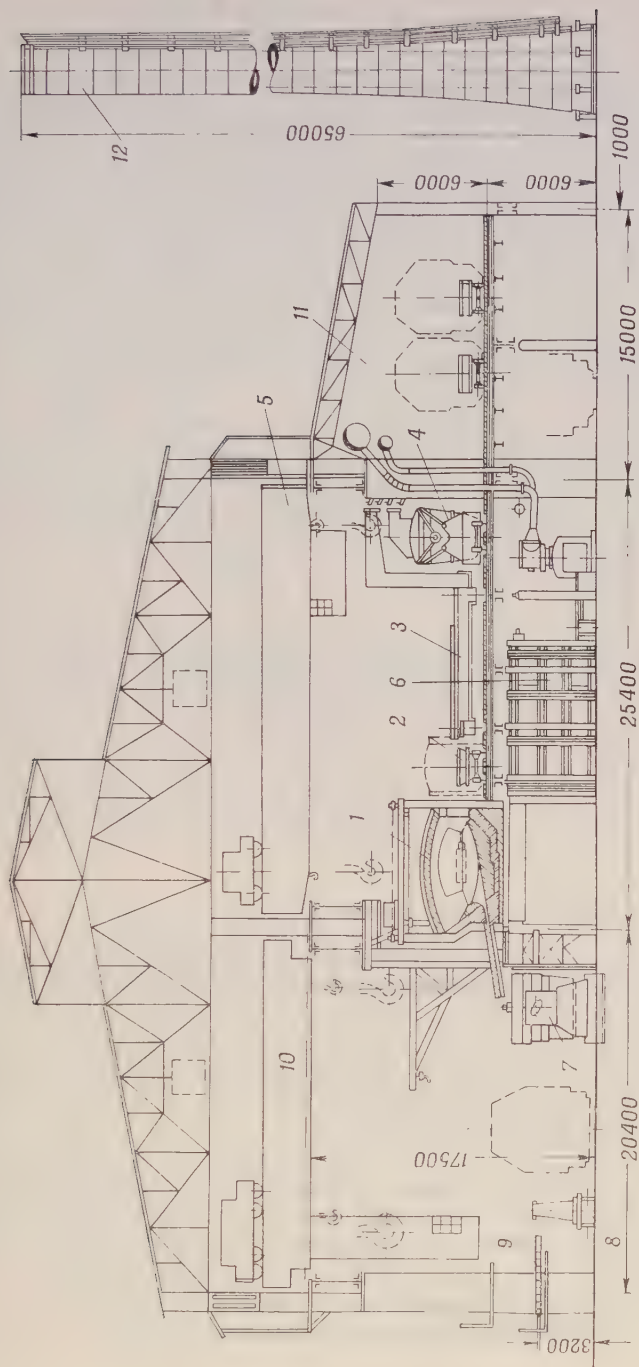


Fig. 62. Diagrammatic section of a modern open-hearth plant.

1 - furnace; 2 - charging box; 3 - ladle; 4 - hot-metal transfer car; 5 - overhead travelling crane; 6 - regenerators; 7 - steel
 ladle; 8 - pouring platform; 9 - ladle; 10 - ladle; 11 - crane on the pouring side; 12 - stack

Some economy of scarce and highly calorific coke-oven gas may be effected through the use of natural gas, in which case more blast-furnace gas has to be added to the mixture. The gas mixture may have a calorific value of 1500 to 3000 kcal/normal cu m. In the liquid group use is ordinarily made of residual-oil fuel. It is mainly utilised by non-integrated steel works which have no supply of blast-furnace gas of its own. The current trend in the Soviet Union is to change over such works to natural gas.

In the case of gaseous fuels, the principal combustible components are carbon monoxide, hydrogen, methane and the more complex hydrocarbons. Residual oil mainly consists of complex hydrocarbons.

The capacity of an open-hearth furnace is closely related to the quantity of fuel burned in it per unit time. Therefore, both in the design stage and during operation every attempt should be made to raise the rate of fuel combustion. This is usually done by mixing the fuel and air thoroughly, preheating and raising the pressure of the mixture, and reducing the share of inert gases in it. If the fuel is to be fully burned and the bath of metal efficiently oxidised, there must be some excess of air in the mixture compared with the combining proportions. Then the products of combustion will carry some oxygen and an oxidising flame will be obtained. The carbon dioxide and water produced by combustion are also efficient oxidisers. Where the oxidising effect of the flame has to be minimised, less air should be admitted or more fuel added. In both cases, incomplete combustion follows, and the products of combustion carry more reducing agents, such as carbon, carbon monoxide, methane, hydrogen, etc.

33. The Charge for the Open-hearth Furnace

The conversion of pig iron in open-hearth furnaces may be either by "the cold pig and scrap" process or by "the hot pig, scrap and ore" process.

In the pig and scrap process the charge mainly consists of steel scrap (60 to 85 per cent) and pig iron (15 to 40 per cent). The charge is cold. This type of working is most common at non-integrated steel plants having no blast furnaces.

The hot pig, scrap and ore process uses a charge made up of 20 to 60 per cent scrap and 40 to 80 per cent pig iron, the balance (15 to 30 per cent) being hematite ore. The charge is molten, for which reason this variety of the open-hearth process is employed at integrated iron and steel works. The reason for the addition of ore is this. The pig iron carries with it a good proportion of impurities. The oxygen of the blast-furnace gas cannot oxidise all of them or

will do that but slowly. In melting, the ore forms a ferrous slag which speeds up the oxidation of the impurities. The metallic iron reduced from the ore addition increases the steel yield of the furnace. The yield of metal is, therefore, 103 to 107 per cent of the metal part of the charge.

In addition to pig iron, steel scrap and ore, the charge includes limestone or lime. The proportions of the charge ingredients vary with the steel grade desired and the chemical composition of the source materials.

Pig iron. The pig iron used in open-hearth furnaces is of the steel-making variety (see Table 5). Before it is charged into a furnace, molten pig iron is equalised as to chemical analysis and temperature in a mixer.

Steel scrap. This ingredient is classed according to piece size and chemical analysis. The most important point is that the content of harmful impurities must be as low as practicable.

Iron ore. The iron ore added to the charge must be in lump form and contain not less than 55 per cent Fe and the least possible quantity of impurities.

Limestone. This ingredient is used in basic open-hearth furnaces as flux and should be in lumps measuring 25 to 100 mm across. It should carry as little sulphur and phosphorus as possible and contain not less than 49-52 per cent CaO.

Lime must be fresh and lumpy, containing at least 75 per cent CaO.

In acid open-hearth furnaces, quartz sand and crushed silica brick serve as the flux.

In basic open-hearth furnaces, the fluidity of the slag is enhanced by additions of grog, bauxite and fluorspar.

34. The Basic Open-hearth Process

The process may be conveniently divided into the following stages: hearth preparation, charging, melting, refining, and finishing.

Hearth preparation. Before each heat, the furnace bottom is prepared, i.e., patched by shovelling in crushed and calcined dolomite or magnesite which frits into position at the operating temperature. The making up of the banks is begun before the steel is tapped. After tapping, the taphole is made up, and the furnace is ready for recharging.

Charging. The solid charge materials, such as ore, limestone, scrap and pig iron, are fed in layers, each layer being heated up before another feed is made. Most often, the bottom is covered with small pieces of scrap or ore, which is followed by limestone, scrap and pig iron. This job is done by a charging machine on the charging floor, and the materials are fed through the charging doors.

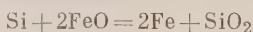
A modern charging machine of the so-called low ground type consists of two main parts: the broad bottom truck driven by electric motors and mounted on flanged wheels which ride a rail track laid along the furnaces; and the charging carriage which travels on a track laid across the bottom truck. This carriage is fitted with a long arm called the charging bar or ram. The charge materials are run to the furnace in charging boxes on bogies. The charging bar is so operated that a charging box is engaged, raised and passed into the furnace where it is turned upside down and the contents deposited. By reversing the sequence, the box is then placed on its bogie again.

Most of the fuel is burned during the charging operation so as to heat and melt the materials rapidly and thoroughly.

Melting. In the cold pig and scrap process, the melting of the scrap is facilitated by the melting of the pig iron above it. Both the heating and melting of the pig iron and scrap oxidise the iron. The impurities in the iron are oxidised directly by the gases and, mainly, by the iron oxides thus formed. By the time the charge is fully molten, the silicon is oxidised almost completely, the manganese to the extent of 60 to 80 per cent, the phosphorus 30 to 40 per cent, chromium 50 per cent, and carbon 25-35 per cent.

In the hot-metal process, molten pig iron is poured into the furnace, and the heat stored up in it appreciably speeds up both the heating and melting of the iron ore and limestone.

In melting, the ferrous oxide of the iron slag oxidises the impurities in the pig iron:



the carbon monoxide produced escaping as a gas.

The carbon monoxide forming in the bath before it is well heated throughout causes the thick and viscous slag to foam. This foaming is utilised for the removal of primary slag by gravity through the slag holes in the rear wall of the furnace or over the dykes in the charging doors—the operation called the runoff. As a result, less lime is required to flux the oxidised phosphorus and silicon, the depth of the slag blanket is reduced, and the metal is heated more efficiently. In large furnaces, the slag is allowed to run off for one or two hours. Table 8 gives the approximate composition of the runoff slag.

Towards the end of the melting stage, the well heated limestone, now transformed into lime, floats to the surface and is dissolved in

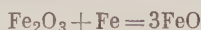
Table 8

Composition of Runoff Slag in the Cold Pig and Scrap Process
(per cent)

Molten pig iron in charge	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	P ₂ O ₅	S
55	38.20	4.60	20.10	2.00	9.50	3.30	17.70	2.20	0.09
60	42.80	4.00	14.80	2.70	13.90	8.20	11.20	1.60	0.10
70	46.30	6.00	16.60	3.20	8.20	3.30	14.00	2.00	0.10
80	48.10	7.20	18.10	1.60	8.40	3.70	8.70	3.00	—

the slag, thereby increasing its basicity and decreasing the content of iron oxides.

The melting stage is followed by the *refining stage* (Fig. 63), during which the oxygen of the slag oxidises the impurities of the iron. The flue gases interact with the metal through the blanket of slag, and the ferrous oxide at the interface between the slag and the air is oxidised to ferric oxide. The latter is carried by diffusion and convection to the surface of the molten bath where it interacts with the metallic iron:



The accumulation of ferrous oxide at the interface between the slag and the metal results in its diffusion from the slag into the metal and the oxidation of the impurities according to the reactions quoted earlier. Some of the ferrous oxide is carried by diffusion or convection back to the interface between the slag and the gas, where it is again oxidised to ferric oxide. In this way, the slag acts as the carrier of heat and oxygen from the gases to the metal.

The oxidation of the impurities is intensified by the addition of some ore at the beginning of the refining stage. The carbon in the bath begins to oxidise to carbon monoxide vigorously, which is accompanied by the boil of the bath as the gas goes through and agitates it. After this "ore boil", the bath should boil for about an hour without any ore additions. During this "lime boil" the steel is worked to the required chemical analysis and degassed. The slag composition at the end of the "lime boil" is given in Table 9. Then the requisite deoxidisers and recarburisers are added, and the metal is tapped.

Being soluble both in slag and metal, the ferrous oxide continuously travels back and forth:

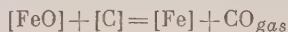


Table 9

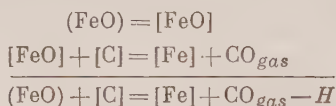
Slag Composition at the End of the Lime Boil

Steel tapped	Fe ₂ O ₃	FeO	MnO	SiO ₂	CaO	MgO	P ₂ O ₅	CaO/SiO ₂	Works
Mild	—	13.40	15.7	20.2	38.2	8.5	1.0	1.90	Magnitogorsk
Mild	—	11.80	8.9	24.2	41.7	11.0	1.2	1.78	Kuznetsk
Carbon	—	15.20	15.0	18.5	45.2	2.9	0.9	2.45	Kuznetsk
(0.36% C)									
Carbon	—	11.00	11.5	20.4	43.7	8.5	1.0	2.14	Kuznetsk
(0.4% C)									
Medium-alloy	0.41	8.76	10.9	18.9	46.6	10.6	1.4	2.46	Kirov

On entering the metal, the ferrous oxide oxidises the carbon dissolved in the metal:

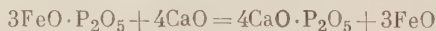


The overall oxidation of the metal by the ferrous oxide of the slag is an endothermic reaction:



The higher the temperature of the bath, the greater the amount of carbon burnt. Simultaneously, the metal is raised in temperature, so that when the carbon content has been reduced to the desired level, the steel is sufficiently hot and fluid for tapping.

The repeated flushing of slag in order to remove the phosphorus may well continue throughout the refining stage. All of the phosphorus may be considered to have been removed when its content in samples taken after flushing does not exceed 0.01-0.02 per cent. The high temperature of the bath and the reducing action of the carbon would reduce the phosphorus from the oxides in the slag, and the metal would absorb it. To prevent this, the oxidised phosphorus in the slag is made to combine with lime. In high-lime slags, calcium phosphates may form through the substitution of the ferrous oxide of iron phosphate with lime:



In order that the phosphorus of the slag may be reliably combined into calcium compounds, the basicity $\left(\frac{\text{CaO}}{\text{SiO}_2}\right)$ of the slag is continually increased to 2.7-3.0 towards the completion of the heat.

Sulphur being a harmful impurity, its content in steel must be kept down to 0.05-0.02 per cent. In basic open-hearth working, the sulphur is slagged in the form of manganese and iron sulphides according to the reaction:

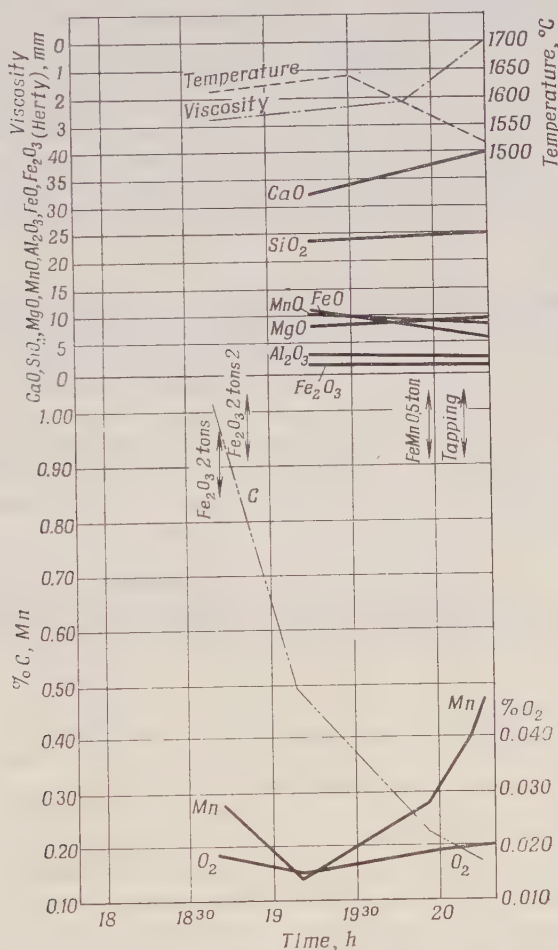


Fig. 63. The progress of the refining stage in the basic open-hearth process

The sulphides interact with the lime according to the reaction:



and



These reactions produce calcium sulphide insoluble in metal. The stringent requirements as to the sulphur content of steel and the difficulty with which sulphur can be removed from it call for thorough control of the charge materials, if a steel of high quality is to be manufactured.

35. Deoxidation of Open-hearth Steel

The reactions that take place when open-hearth steel is deoxidised by ferroalloys are similar to those occurring in Bessemer working. In the manufacture of plain carbon steels, ferromanganese is added to the bath in an amount just sufficient to obtain the lowest prescribed content of manganese. After 5 to 7 minutes, blast-furnace ferrosilicon (9-13 per cent Si) is added to the bath in a quantity required to obtain 0.1-0.15 per cent Si in the steel. The silicon interacts with the ferrous oxide dissolved in the metal and the manganous oxide produced by the addition of ferromanganese. As a result, composite silicates of the type $n\text{FeO} \cdot m\text{MnO} \cdot q\text{SiO}_2$ are formed. They have a lower melting point, a higher fluidity and a lower specific gravity than molten iron. Therefore, they float to the surface in globulets which may coalesce into larger globules.

Finally, 45-per cent or 75-per cent ferrosilicon additions are made to the ladle or, which is better, into the tapping spout on tapping, and aluminium may be thrown into the ladle to complete the deoxidation and to fix the dissolved gases. The quantity of ferrosilicon must be enough to obtain the desired content of silicon in steel and to make up for its burn-up which may be as high as 15 to 25 per cent. Aluminium additions usually amount to 100-400 grams per ton of steel. The total amount of deoxidation products is negligible, and they form submicroscopic structures dispersed throughout the volume of the metal. The resultant alumina appears as hard crystals of corundum (Al_2O_3) which may serve as crystallising nuclei during the solidification of the steel. This property is utilised for control of the grain growth in steel ingots: varying the quantity of aluminium addition will change the grain size.

Deoxidation is most efficient with composite deoxidisers like silicomanganese, silico-spiegel or AMS alloys containing aluminium, manganese and silicon. Steel may be alloyed with both ferroalloys and pure metals. Easily oxidisable additions, such as ferrochromium, are made to enter deoxidised steel.

36. Rimming Steel

Rimming steel is steel that has not been deoxidised in the furnace or the ladle. It is deoxidised in the mould due to the interaction of the carbon of the steel with the oxygen dissolved in the latter according to the reaction:



In solidifying, a solid rim of clean metal is rapidly formed next to the mould walls, increasing the concentration of carbon and oxygen in the core. This and the drop in the temperature promote the above reaction in the forward direction. The carbon monoxide forms bubbles at the interface of the solid and the molten phases. As the reaction progresses, the bubbles grow in size, break away and float. The bubbles move away from the mould sides, towards the ingot core and upward. On their way, the bubbles continue to grow in size, for the reaction at the interface between the gas and the metal also develops in the forward direction. The evolution of carbon monoxide during solidification produces a quiet boil in the mould, driving out some of the dissolved gases and impurities into the core of the ingot. No pipe can form in a rimming steel ingot, but the core is porous. These pores, or blowholes, coalesce together during rolling. Only low-carbon steel (not over 0.3 per cent carbon) can be made to rim.

Rimming steel is cheaper to make as it uses no expensive ferroalloys for deoxidation. This is why up to 80 per cent steel is manufactured as rimming (or, in U.S. usage, rimmed). Furthermore, rimming steel has no non-metallic inclusions usually produced by ferroalloys. This is an important consideration in sheet-rolling and deep drawing, for in sheet, non-metallic inclusions may appear on the surface and provoke corrosion, while in drawn articles they may give rise to cracking and tears. Therefore, sheet is mostly rolled from rimming steel.

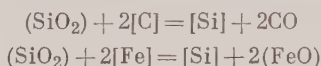
37. The Acid Open-hearth Process

The process usually consists of the following stages: hearth preparation, charging, melting, the "melt-out", the boil, and the finishing operations.

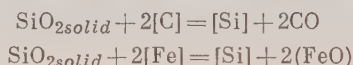
The acid open-hearth furnace is similar to the basic type, except that its lining is of silica brick, and the bottom and banks are fritted with quartz sand. Because of the acid slag used, phosphorus and sulphur are not eliminated, and the charge materials and fuel should carry no impurities. A quality charge will make a high-quality steel in the acid open-hearth furnace.

The slag forming in the melt carries about 45-48 per cent SiO_2 and 50-54 per cent ($\text{FeO} + \text{MnO}$). As the melting progresses, the SiO_2 concentration increases to 55-60 per cent due to the dissolution of the patchwork and the reduction of FeO and MnO from the slag. Though the slag is high in ferrous oxide (20-35 per cent), its oxidising action is weaker, and the impurities and carbon are oxidised less vigorously than in the basic process. The boil is built up by small but frequent ore additions.

Among the features of this process special mention should be made of the oxidation and withdrawal of the silicon as SiO_2 into slag at the beginning of the heat and the reduction of the silica from the slag during the boil. The silica is reduced by carbon, manganese and iron according to the reactions:



More silica is reduced with temperature rise, and some of it may be reduced from the lining according to the reaction:



The reduction of the silica from the bottom by the carbon of the metal greatly facilitates the burning out of the carbon, degassing and stirring. Most of the silica and manganous oxide is reduced during two or three hours before tapping.

Where furnaces are run at high temperature, the silicon and manganese content is decreased to 0.35-0.6 and 0.36-0.4 per cent, respectively, without ferrosilicon and ferromanganese additions. The resultant steel requires little amounts of deoxidisers, if at all.

38. Quality, Properties and Uses of Acid Open-hearth Steel

The deoxidation of the molten metal by reduced silicon improves the quality of the resultant steel in that non-metallic inclusions in it are very few and far between.

The acid slag prevents the molten metal from absorbing hydrogen and nitrogen, and the mechanical properties of acid open-hearth steel are higher than those of basic steel. Anisotropy, i.e., difference in properties in different directions, in acid steel is less pronounced, but the steel is more expensive (by 50 to 100 per cent) to make than the basic variety and is therefore employed for the manufacture of critical products (guns, shafts, high-quality sheet, etc.). Acid steel may be alloyed with various elements and offers an advantage in that the burning losses of the alloying elements in an acid open-hearth furnace are less than in basic furnaces.

39. Economics of the Open-hearth Process

Open-hearth furnaces are classed according to their daily output per square metre of bottom area. In the Soviet Union, there has been a steady increase in furnace output. While in 1932, the average capacity for basic furnaces was 2.68 t/sq m, the current figures average 7 or 8 t/sq m, rising as high as 10-11 t/sq m in some cases. In 220-260-ton furnaces a heat usually lasts for 7 to 10 hours, and the fuel consumption (in equivalent fuel) is 130 to 150 kg/ton.

The daily output of a given furnace greatly depends on the operator's efficiency, heat utilisation, and improvements in furnace design. The latter factor has a direct bearing on how long a furnace may last before it has to be shut down for repair. One such refinement is the use of suspended arched roofs in basic materials which are much more durable than silica brick. Timely and skilled preventive maintenance also goes a long way towards extending the service life of a furnace.

The staff of furnace attendants is usually small, as furnace operation has now been fully mechanised.

40. Oxygen Enrichment of the Open-hearth Furnace Blast

The use of a blast with oxygen enrichment appreciably speeds up the open-hearth process.

At the present time, some of the Soviet steel works employ a blast enriched with as much as 25 to 35 per cent oxygen, which totals 30 to 65 cu m of oxygen per ton of steel produced.

Among the advantages offered by oxygen enrichment in the blast are: better heat utilisation in the bath, reduced heat duration (by a third to two-thirds), increased output, and reduced fuel consumption. For a 100-ton furnace blown with 29 to 30 per cent oxygen, the time of a single heat has been reduced from 9 h to 3 h 30 min, the daily output increased 2.5 times, and the fuel consumption reduced from 150 to 92 kg per ton of steel produced, the oxygen requirements being 55 to 70 cu m per ton.

If oxygen enrichment is to be properly utilised during charging and melting, it is important that the charging equipment and crew operate without a hitch. As this involves a higher rate of work, automatic control seems to be more reliable, especially as far as combustion and hearth temperature are concerned.

Oxygen enrichment is also advantageous in that fuels of low calorific values may be burned. In addition, the oxygen blast can be employed during the refining stage for the direct oxidation of the impurities. Even a short blow with oxygen cuts down smelting

time by 30 to 60 minutes and saves 5 to 6 per cent fuel in large furnaces.

Current practice favours the oxygen blast blown through water-cooled tuyeres, or lances, located in the roof, as it can be easily automated.

If precaution measures are not taken, the oxygen blast, unfortunately, causes the metal and slag to sputter heavily. On top of it, the extremely high temperature around the oxygen impact area results in the vaporisation of much iron. The two factors seriously aggravate the dust problem. While under normal conditions the dust content during the refining stage is 1.5-2 grams per cubic metre of flue gas, the oxygen blow increases the figure to 16-20 grams per cubic metre.

Sputter can be conveniently controlled by means of a rifled-bore nozzle provided in the oxygen lance. The jet of oxygen issuing from the tip "screws" into the bath, and sputter is almost non-existent. The vaporisation of iron can be controlled by making heat-absorbing additions to the bath in the area where the oxygen blast is admitted.

41. Automatic Control of the Open-hearth Furnace

Automatic control of the open-hearth furnace covers fuel combustion, maintenance of gas pressure above the bath, heat supply, and valve operation.

Each of these elements of automatic control increases daily output, reduces fuel consumption, and prolongs furnace service life. The ultimate in improvement is attained where all of these elements are integrated into a comprehensive control system. At present, all open-hearth furnaces in the Soviet Union are controlled automatically.

Automatic (programmed) control of heat supply operates as follows. The furnace requires different quantities of heat at the various stages of its operation. During the stages requiring much heat, fuel mixtures of high calorific value should be burned, while those of low calorific value may well do when the requirements in heat are reduced. These varying requirements are embodied in a programme which is followed by controllers metering out the requisite quantities of blast-furnace and coke-oven gases and air. The controllers are connected by linkages. When the setting cam of one of the controllers is rotated through an angle, the cams of the other controllers are also rotated through the same angle. The cams have lobes of complex shape and of varying radius. So, their position varies the lift of the butterfly valves in the air and gas intakes according to the cam settings. The operator can "override"

the controllers in order to add more heat (or reduce heat supply) with the aid of a master switch.

The pressure of the flue gases above the bath should be such that no cold air is drawn in from the atmosphere. It is maintained by a controller built around an electric bell-type differential pressure gauge. The setting of the controller varies from stage to stage as a function of the fuel flow rate. The gauge, which acts as the sensing element of the controller, has one tube placed in the furnace roof and another placed outside. When the pressure differential deviates from the set point, the signal from the controller is fed to an electric hoist (the actuator), and the latter operates a damper (the final control element) so as to minimise the "error", i.e., the deviation from the desired pressure.

The valves are automatically operated by a contact galvanometer which "senses" the temperature of the checkerwork in the respective air regenerator chambers. In addition to it, there is a timer which will cause the valves to reverse the flow of air not earlier than 3 minutes and not later than 10 minutes after the previous reversal, though the temperature difference may be other than the preset one. Another temperature sensing element feeds a signal to the controller in case the roof temperature has reached the safe limit. In response, the controller reduces the quantity of heat admitted into the furnace. If this fails to reduce the roof temperature, the valves are operated to reverse the flow of the air through the regenerators ahead of schedule.

C. THE ELECTRIC PROCESSES

The electric furnace has a number of advantages over the open-hearth furnace. For one thing, there is the possibility of securing any desired temperature, thus providing a means of making refractory alloys and using refractory basic slags which remove more sulphur. For another, there is no flame, and the atmosphere in the electric furnace may be made reducing or neutral, at will. Furthermore, the high temperature and the reducing atmosphere produce highly basic slags low in ferrous oxide (0.2-0.5 per cent FeO). As a result the burning loss of alloying elements is appreciably reduced, and the metal can be efficiently deoxidised by removing FeO from the metal into the basic slag. The steel made in the arc furnace is better deoxidised than in the open-hearth furnace. Finally, a great variety of steels, differing in carbon content and with any content of alloying elements, can be manufactured in the electric furnace.

Two principal types of electric furnace are used in steelmaking. These are the direct or arc-resistance type and the induction type.

42. The Direct or Arc-resistance Furnace

Modern arc-resistance furnaces generally use three-phase alternating current, and have vertical carbon or graphite electrodes, and a non-conductive hearth. The current arcs from the positive electrode to the slag, is conducted through the metal charge back to slag blanket and arcs again to the negative electrodes.

Arc-resistance furnaces have capacities up to 180 tons, and those with a capacity of 250 to 270 tons are in the development stage.

An arc-resistance furnace (Fig. 64) consists of a metal cylindrical body, a flat or spherical bottom, and a swinging roof. On the inside the furnace is lined with refractory materials. The lining may be either basic or acid. In basic practice, the bottom is made up of two or three courses of magnesite brick over which a layer of magnesite or dolomite 150 to 200 mm thick is rammed into place. In the case of acid lining, silica brick form the walls and supporting brickwork, while the hearth is covered with quartzite. Basic-lined furnaces are most common.

The basic-lined hearth will give a service life of 1500-2500 heats, and the walls 100-150 heats.

The cylindrical part of the body has a slagging door and a pouring spout. The body is carried by two sectors which are set up in a frame mounted on a foundation. The sectors and furnace have a tilt of 40 to 45° for pouring; the tilt of 10-15° serves in flushing the slag through the slagging door.

The furnace is powered by a step-down transformer which brings down the voltage from 6-30 kV to 80-280 V. The transformer may have from 3 to 12 taps on the L.V. side for better control of electric supply and heat conditions of the furnace. The rating of the transformer ranges from 1 to 15 MVA for furnaces of 1 to 40 tons capacity. The specific rating progressively decreases to 250 kVA/ton with furnace capacity increasing to 180 tons (Table 10).

Table 10

Arc-resistance Furnace Data

Nominal capacity, tons	Actual charge, tons	Transformer rating, kVA	Max. current, A	Specific rating, kVA/tons
5	9	2250	4200	450/250
10	13	3500	—	350/270
15	19.6	6000	13,000	335/255
30	37.0	9000	15,000	335
45	50	15,000	18,700	267
80	90-95	25,000	23,200	312
180	—	45,000	34,500	250
250	—	60,000	—	—

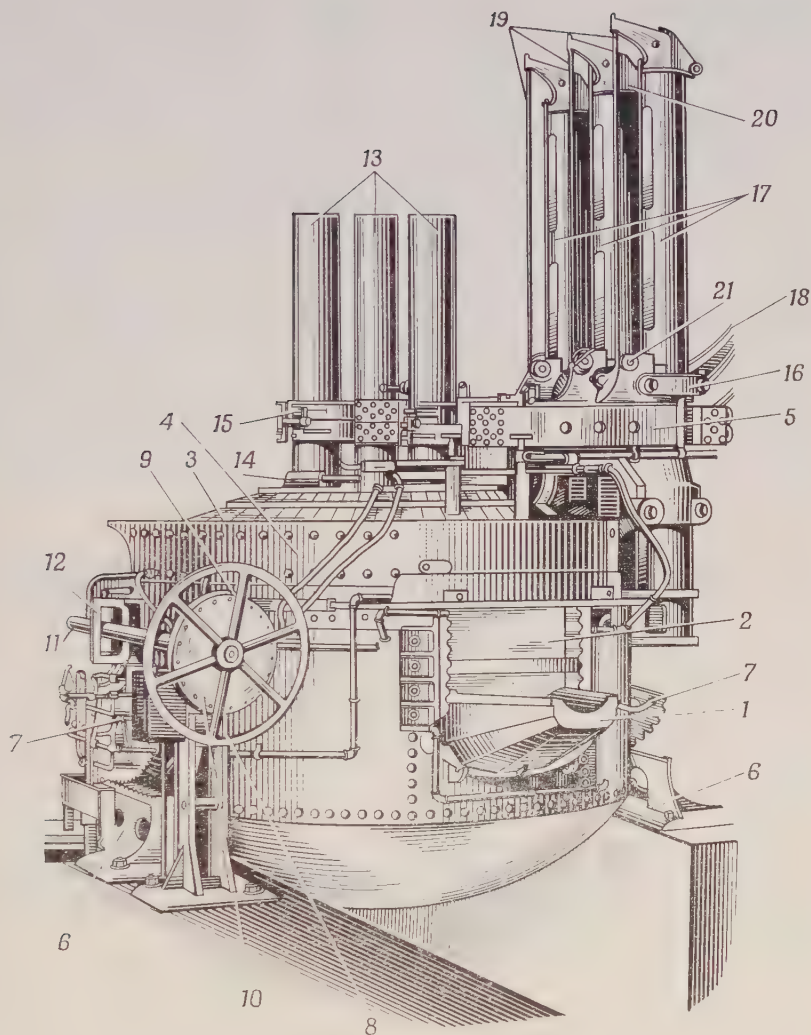


Fig. 64. Three-phase arc-resistance furnace:

1—pouring spout; 2—door; 3—roof; 4—roof support; 5—electrode crosspieces; 6—racks; 7—tilting pinion; 8—handwheel; 9—rotating motor; 10—gearbox; 11—tube; 12—frame; 13—electrodes; 14—water-cooled sealing rings; 15—clamps; 16—sliders; 17—columns; 18—copper cable; 19—steel rope; 20 and 21—sheaves

Medium and large furnaces are charged mechanically. The more usual method is to use a charging machine or chutes, both working through the door (door-charge furnaces). A more recent method uses a crane-operated clamshell bucket or net; the roof and electrodes together are swung aside, and the materials are dropped from the top (top-charge furnaces).

43. Arc-furnace Processes

Steel in arc furnaces may be refined with or without oxidation. Oxidation may be dispensed with where the metal ingredients of the charge are close to the desired steel grade in analysis. In such cases, a reducing slag is used both in melting and refining (single refining or single-slag practice). Usually, this process is employed to smelt alloy wastes to alloy steels. In working with oxidation (double refining or two-slag practice), the charge is molten and refined under an oxidising or black slag; then the black slag is removed and a reducing or white slag is formed under which refinement is completed. Under such conditions, phosphorus and/or carbon can be eliminated almost completely.

Double Refining (or two-slag working). The melt-down stage uses the highest power input (the highest voltage of the transformer) to speed up melting. A back charge of lime (2 to 3 per cent of the metal's weight) is spread over the scrap. The lime speeds up slag formation, and the slag thus formed stabilises the arc and protects the bath from the carburising effect of the electrodes and gas absorption.

The oxidising slag is formed by the lime and iron ore (usually 1 per cent each) added to the furnace before the charge is molten. At the end of the melt-down stage, the carbon content must be 0.5 per cent higher than is prescribed for the finished steel, and the phosphorus content must be not over 0.04 per cent. Ten or fifteen minutes after the ore additions are made to the furnace, 60 to 70 per cent of the slag is flushed. This slag withdraws most of the phosphorus as iron phosphates.

Then lime (1 to 1.5 per cent by weight of the metal) is added to the furnace, the metal is heated, and several feeds of iron ore and lime are made. As the temperature of the bath increases, more carbon is oxidised, causing the bath to boil. The boil drives out the gases and non-metallic inclusions.

For better phosphorus removal, the slag is flushed more than once. The foamed slag forming during the boil is removed by gravity. During this stage the phosphorus is oxidised to the pentoxide (P_2O_5) which forms calcium phosphate, and the latter becomes a constituent of the slag:



With the slag replenished repeatedly, the phosphorus content of the metal may be reduced from 0.04 to 0.01 per cent.

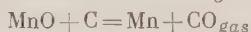
The oxidising slag is called "black" due to the colour it is given by the iron oxides.

After the carbon content in the metal has reached the lower specified limit and the phosphorus content has been reduced to approximately 0.015 per cent, some 80 per cent of the slag is flushed, and the bath is allowed to boil without ore additions for 25 minutes. Then all of the oxidising slag is removed before the reducing stage is commenced.

The purposes of the reducing stage are (1) to deoxidise the metal; (2) to eliminate the sulphur; (3) to finish the steel to the specified composition; and (4) to heat the metal.

After the oxidising slag has been removed, a reducing slag is formed from lime, fluorspar and coke breeze.

The carbon of the coke reduces the ferrous and manganous oxides of the slag:



As more ferrous oxide is reduced, a white reducing slag is formed with the following approximate analysis (in per cent):

CaO	MgO	SiO ₂	Al ₂ O ₃	FeO	MnO	CaF ₂	CaS
50-60	10-12	15-20	2-3	max. 1.5	max. 1.5	5-10	1.0

The deoxidation of the slag by carbon and then of the white slag by crushed ferrosilicon or aluminium produces a well deoxidised steel. Slag deoxidation is favourable for the diffusive deoxidation of the metal, as the ferrous oxide is continually withdrawn from the metal into the slag. With deoxidisers added to the slag, no non-metallic inclusions develop in the steel.

The low content of ferrous oxide and the high content of lime in the slag promote sulphur removal from the metal into the slag in the form of CaS.

Carbon steel is refined under calcium-carbide slags which are more efficient reducing agents than other slags. A calcium-carbide slag is formed from the ordinary white slag when more coke is added to the slag-forming mixture consisting of lime, fluorspar and coke breeze. To obtain a calcium-carbide slag, a reducing atmosphere is created in the furnace and the power input is raised to the utmost (the transformer is changed to the highest tap on the H.V. side). As a result, calcium carbide is formed according to the reaction:



The calcium-carbide slag has the following approximate composition (in per cent):

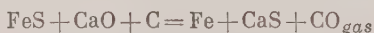
CaO	MgO	SiO ₂	Al ₂ O ₃	FeO	MnO	CaS	CaF ₂	CaC ₂
55-65	8-10	10-15	about	about	about	about	8-10	1-5
			2	0.4	0.2	2.0		

The slag owes its increased reducing quality to the lower content of iron oxides and the presence of calcium carbide—a very powerful deoxidiser.

Deoxidation by calcium carbide proceeds according to the reaction:



Working under a calcium-carbide slag eliminates much of the oxygen in the metal, and the sulphur is withdrawn into the slag as follows:



During the reducing stage the sulphur content can be brought down to 0.01 per cent or even a few thousandths of one per cent.

The duration of a double-refining heat is usually 7 or 8 hours.

Single Refining (or single-slag practice). Refining under a single (reducing) slag may be employed when the charge contains much alloy scrap, and oxidation would burn some of the valuable alloying elements. In single-slag practice, the metallic charge must contain less phosphorus than is allowed for the finished steel, as no phosphorus is withdrawn from the metal. When molten, the bath should be very close to the specified analysis. The charge for single-slag working usually consists of 70-80 per cent alloy scrap and 30-20 per cent mild iron which is added to control the carbon content.

The slag-forming materials are fed into the furnace during the melt-down stage, and refining is completed under white or carbide slags.

A single-slag heat is usually one or two hours shorter than in two-slag practice, giving an increase of 20-25 per cent in daily output and a decrease of 10-15 per cent in power consumption.

Single-slag practice suffers from a series of drawbacks, the principal among which are (1) excessive carburisation in some cases due to the reducing carbide slag; and (2) more occluded gases and impurities as there is no boil to allow their escape. For this reason, some high-quality steels intended for vital applications cannot be produced by single-slag working.

Acid Working. Acid-lining working uses acid slags which remove no phosphorus or sulphur. Therefore, the scrap used in acid practice should contain not more than 0.03 per cent sulphur and 0.03 per cent phosphorus. The slag covering the molten metal carries 38-46 per cent SiO_2 , 6-7 per cent CaO , 18-26 per cent MnO , and 22-28 per cent FeO .

For the removal of occluded gases, the vigorous boil of the bath is equally important in acid and basic practice. In the acid-lined furnace, however, it is handicapped by the fact that the ferrous oxide of the slag is combined with the silica as ferrous silicate ($2\text{FeO} \cdot \text{SiO}_2$) and so carbon monoxide is produced but slowly. Furthermore, the slag is thick and pasty, and the temperature of the bath has to be raised considerably.

The FeO content of the oxidising slag should be anywhere between 30 and 35 per cent and is maintained by additions of iron ore (about 2 to 4 per cent of the charge). As the carbon burns out, the content of ferrous oxide in the slag drops to 15-17 per cent. In most cases, the slag is replenished by partly flushing it and by adding fresh grog, foundry sand, and lime.

44. Economics of the Arc-resistance Furnace Process

Several charges are usually needed to build up the bath, and for furnaces up to 35 tons in capacity the charging occupies 15 to 35 minutes. Apart from furnace capacity, the charging time is dependent on whether the furnace is charged by hand or mechanically. A typical door charging machine does the job at the rate of half a ton per minute. For a 35-ton furnace this works out to one hour. Top-charge furnaces take but a few minutes to fill.

The melt-down period in basic-lined furnaces lasts for from 2.5 to 3.5 hours. The oxidising stage takes 40 to 80 minutes. The reducing stage is about 1.5 hours for plain steels and 2 to 2.5 hours for alloy steels. The total tap-to-tap time for an arc furnace 30 to 35 tons in capacity is 6 to 8 hours for two-slag working and 5 to 6 hours for single-slag practice.

The performance of arc furnaces is assessed in terms of daily output in tons per 1000 kVA of power. Daily output is a function of nominal furnace capacity, working conditions, and the process adopted. On the average, it is 13 or 14 tons per 1000 kVA. Energy consumption is likewise governed by the three above factors and amounts to 500-700 kWh per ton for carbon steel and up to 1000 kWh per ton for alloy steels. Graphite electrode consumption varies between 6 and 9 kg per ton, and that of carbon electrodes between 15 and 18 kg or more.

45. The Induction Furnace

Ferrous metallurgy mostly uses what is known as the coreless (or high-frequency) induction furnace. The assembly of this type consists of a crucible within a water-cooled copper coil and a framework on supports arranged for tilting in pouring. The primary circuit is formed by the coil, and the secondary circuit is the crucible or, rather, the charge in it. The lines of magnetic force link through the charge and induce eddy currents in it, and the latter generate heat.

Commercial induction furnaces built in capacities of 5 to 15 tons operate on frequencies from 500 to 2500 cycles, though large furnaces may use 50 cycles, with an inductor-type generator as standard equipment. Powering is 1 to 0.3 kW per kilogram of charge and increases with decreasing furnace capacity.

In induction furnaces, the slag is heated only by the bath, and this may be not enough for it to melt. For this reason, slag-assisted refining is out of the question, and the melting of charges of clean metals and alloys of known analysis is the principal field of the coreless induction furnace. Limited oxidation, high temperature, intimate stirring, and no electrodes to carburise the melt all serve to produce alloy steels and composite alloys extremely low in carbon. Nevertheless, the induction furnace has yet found a limited field of application as it is less attractive economically and in output than the arc furnace.

The melting of the charge in the induction furnace, the pouring and solidification of the molten metal may all be assisted by a vacuum. Compared with ordinary practice, vacuum working results in a metal containing considerably less occluded gases.

46. Duplex Processes

The possibility of combining the advantages of two processes with the elimination of their respective drawbacks has led to the successful use of duplex processes.*

In a duplex process, an acid Bessemer converter may be ganged with a basic open-hearth furnace. Then, a heat is blown in the converter to virtual elimination of the impurities except for the phosphorus. The metal is then poured into the open-hearth furnace which removes the phosphorus and finishes the metal to the desired quality.

In another arrangement, a basic Bessemer converter may be duplexed with a basic open-hearth furnace. Then, the phos-

*In Soviet usage, the term "duplex processes" applies to any combination of two steel-making processes.—*Ed.*

phorus will be eliminated in the converter, and the other impurities in the open-hearth furnace.

In a still another arrangement, a basic open-hearth furnace may be coupled with an acid open-hearth furnace to produce high-grade steel. The basic furnace will eliminate nearly all phosphorus and reduce the sulphur content, while the acid furnace will remove the gases and deoxidise the metal.

In all arrangements the duplex method effects a considerable economy in the time necessary for treatment in the open-hearth furnace and improves the quality of the finished steel.

47. Utilisation of Complex Ores

A complex ore is one from which two or more metals may be profitably extracted. One such ore is brown iron ore which contains 0.03-0.04 per cent vanadium. The metal vanadium is a valuable and vital material to such a degree that even low percentages are commercially attractive to recover.

In titanomagnetite, vanadium runs 0.1 to 0.5 per cent and as much as 0.5 to 0.6 per cent in the pig iron smelted from this ore. In the acid Bessemer converter where the pig iron is refined the vanadium is oxidised to V_2O_5 and becomes a constituent of the slag. The quantity of slag flushed from the converter amounts to 2 or 3 per cent of the pig iron (by weight), and the V_2O_5 content in the slag increases to 10-16 per cent. The slag is treated for the recovery of the vanadium, and the partially refined pig iron is converted to steel in an open-hearth furnace. So, extraction of a valuable by-product has resulted in the use of the duplex process (the acid converter and the basic open-hearth furnace).

48. Ingot Production

Casting into Moulds. Steel is cast into ingot moulds on the pouring side or the casting floor of a steel-making plant. Upon solidification, ingots are either rolled or forged to shape. Casting into foundry moulds is usually employed in the foundries of engineering works.

The metal or casting ladle consists of a shell fabricated from steel plate and lined with firebrick. For stiffness, the ladle is girdled by rings and ribs. The middle ring, or trunnion belt, has two trunnions for manipulation by a ladle crane. In the ladle bottom there is a perforated brick fitted with a nozzle. In pouring, the nozzle is opened and closed by a leverage-operated stopper.

The stopper consists of a firebrick stopper-end screwed onto an iron rod enclosed in firebrick tubes or sleeves as a protection against molten metal.

After it has been tapped from a furnace, the metal is held in the ladle for 5 to 10 minutes in order (1) to equalise the composition of the steel; (2) to allow the non-metallic particles produced by deoxidation or spalls from the lining to float; and (3) to allow the occluded gases to escape. Then a crane moves the ladle to the ingot moulds which may be either set up on ingot casting bogies, or in the casting pit.

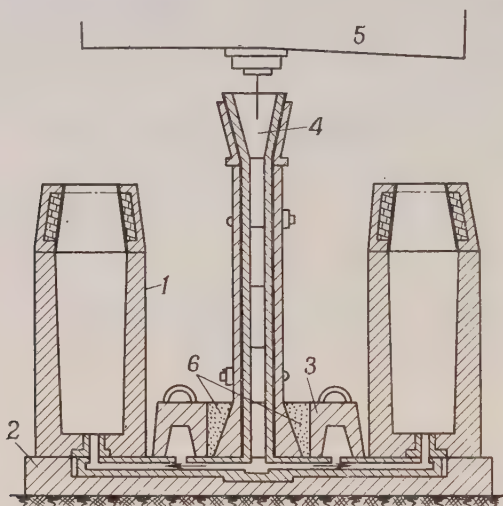


Fig. 65. Bottom-pouring arrangement:

1—mould; 2—bottom plate (or mould stool); 3—slag catcher; 4—fountain or trumpet; 5—ladle; 6—refractory ramming

Pouring may be either top or bottom. In the former case, the ladle is emptied directly into a mould. In the case of bottom pouring (Fig. 65) the molten metal from the ladle runs down a centrally located fountain or trumpet and fills the mould through a runner and bottom outlets. One trumpet can be designed to supply steel to several moulds at a time, and fewer defects are present than in top-poured ingots. On the other hand, top pouring may use a cooler steel and produces ingots containing less non-metallic inclusions. The choice usually depends on the conditions prevailing in the plant. The primary objective in either case is to produce an ingot which would be uniform throughout both in structure and composition.

In solidifying, steel contracts by as much as 8 per cent in volume. This inevitably results in a large and deep central shrinkage cavity in the ingot, called a pipe, which extends almost to the top of the

ingot. The size and shape of the pipe greatly depends on the temperature and rate of pouring, as well as the weight and shape of the ingot. In order to decrease the depth of the pipe some ingots, especially of high-grade steels, are cast in wide-end-up moulds with heat-insulated mould stools (or mould bottom plates).

Ingots are cast in weights from 1 to 20 tons, heavier ingots being used far more seldom. Ingots to be rolled into shapes are square or rectangular in section, and those to be rolled into plate or sheet are flat.

Vacuum-degassing. Increasingly more ground is being gained by casting steel under a vacuum in spite of the fact that the method uses specialised equipment (Fig. 66). The method is a "must" where

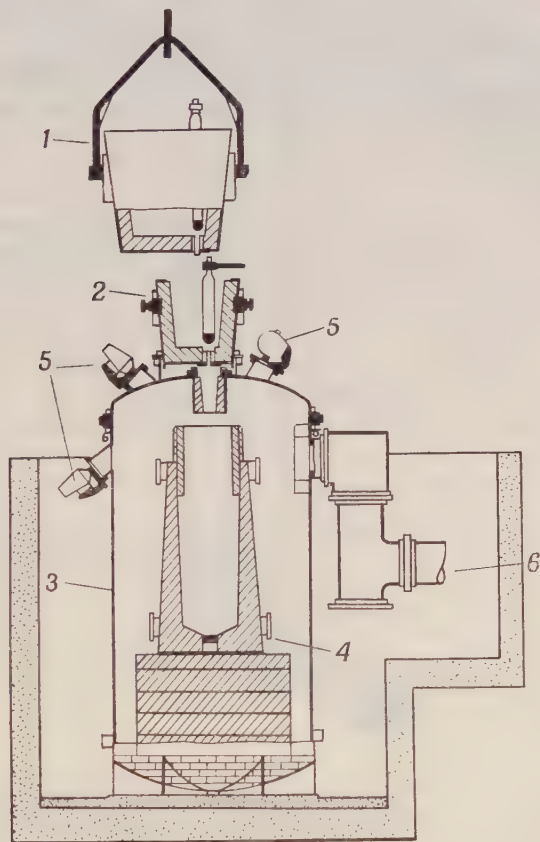


Fig. 66. Vacuum-degassing casting practice:

1—steel teeming ladle; 2—tundish; 3—vacuum degassing chamber; 4—mould; 5—TV cameras; 6—gas off-take

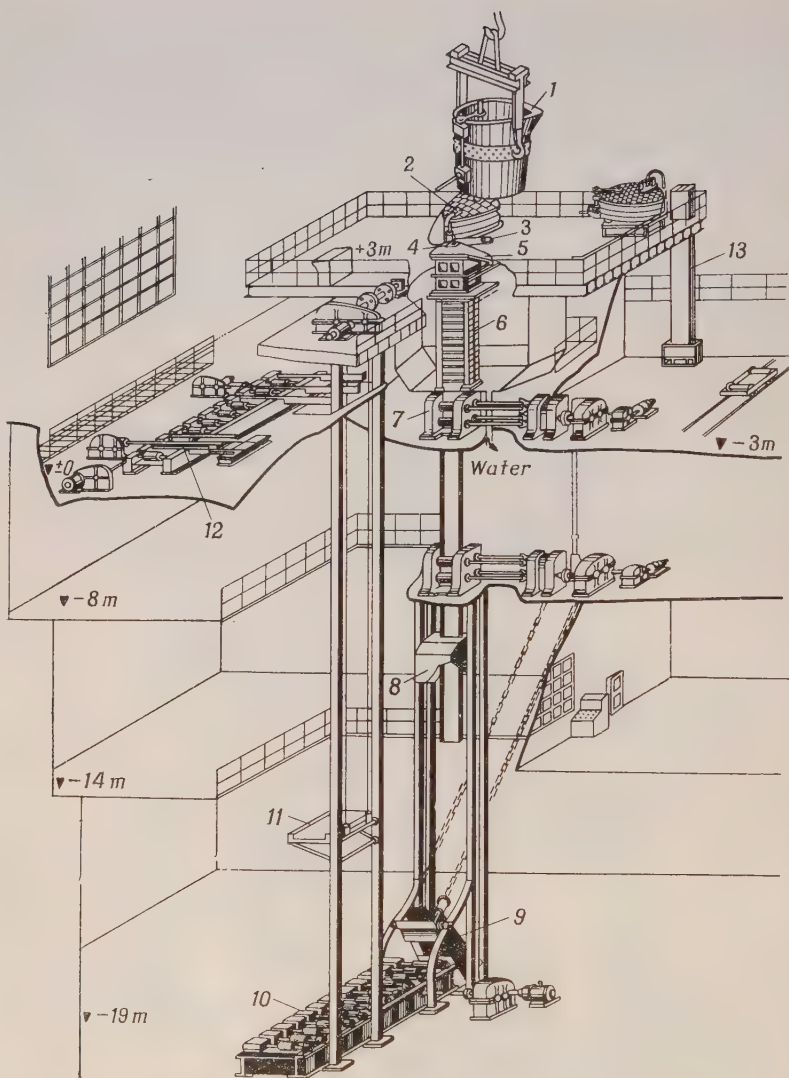


Fig. 67. Continuous casting machine:

1—casting ladle, 10-ton capacity; 2—tundish, 2-ton capacity; 3—mould lubricator; 4—nozzle heater; 5—mould; 6—secondary cooling; 7—withdrawal rolls; 8—strand cutting unit; 9—strand take-up; 10—run-out rolls; 11—elevator; 12—roller-table to storage area; 13—dummy bar

high-grade and special-alloy steels are involved. The vacuum, which usually is 5 to 0.1 mm Hg, efficiently degasses the metal (some 60 per cent of the occluded hydrogen is removed) and decreases the total amount and size of non-metallic inclusions. This appreciably improves the mechanical properties of the steel, especially ductility.

Continuous Casting. A continuous steel casting machine is a vertically arranged unit (Fig. 67). Most of it is placed up to 20 m below the shop floor, and floor space requirements for it are considerably smaller than for a casting pit.

From the casting ladle the steel is emptied into a tundish from which the steel flows in a continuous strand into a mould. The mould is a water-jacketed box of red copper in which the shell of the casting is rapidly formed and the metal solidifies into a dense mass. From the mould, a pair of withdrawal rolls pull the strand at a prescribed rate, while keeping it straight. Between the mould and the outlet from the rolls the casting is sprayed with water. Past the rolls, the solidified strand is cut by an automatic oxy-acetylene or oxy-gas cutter into billets for rolling. A conveyer lifts the billets to the shop floor.

Compared with pit casting, continuous casting is a far more streamlined operation, dispensing with the cumbersome and expensive stock of moulds, bottom plates, and refractories. There is no metal lost, while in casting-pit practice the losses of metal are inevitable. Fewer operators are required to run a casting machine than an ingot casting pit. Furthermore, the metal from a continuous casting machine need not be clogged in a blooming mill. Indeed, heavy-section mills may also be dispensed with sometimes.

Part Three

THE METALLURGY OF HEAVY NON-FERROUS METALS

Chapter VI

THE METALLURGY OF COPPER

49. General

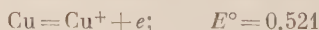
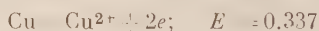
Copper is a lustrous, reddish brown metal. Its crystalline structure is face-centred cubic. Its specific gravity is 8.93. It melts at 1083°C and boils at 2360°C. Copper is remarkably conductive, both thermally and electrically, being second only to silver.

Copper is highly malleable and ductile and is easily rolled into sheet and drawn into wire. It is half as hard as pure iron.

In chemical compounds copper can be uni- and divalent. In acid solutions (CuSO_4), the ions Cu^+ dissociate as follows:

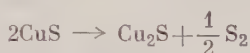
$$2\text{Cu}^+ = \text{Cu}^{2+} + \text{Cu}; \quad K = \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^+}^2} = 1.51 \times 10^6$$

The electrochemical potentials of copper are positive:



Therefore, copper cannot replace hydrogen in acids, and dissolves in the latter only in the presence of oxidisers. Copper does not react with alkaline solutions.

In weathering, a green coating of hydrated copper carbonate mixed with basic copper sulphate forms on the surface of copper. When heated, copper receives a coating of black oxide, CuO , when freely oxidised, or brilliant purplish red Cu_2O when oxidation is restrained. The dissociation pressure of CuO reaches that of oxygen in the air at about 940°C above which the metal can only be oxidised to the protoxide soluble in molten copper. In metallurgical melts Cu_2O displays the properties of a weak base, and forms silicates, ferrites and other compounds with acid oxides. With sulphur copper forms Cu_2S and CuS , the latter tending to dissociate at elevated temperatures according to the reaction:



Copper oxides are readily reduced with as little CO as about 0.01 per cent present in the $\text{CO} + \text{CO}_2$ mixture.

Copper, bronzes and brasses have been used since prehistoric times. The ancients made bronze into tools and weapons, utensils and decorations. Owing to its high resistance to corrosion, copper and brass sheet made an excellent skin for ship hulls and a durable roofing material. Bronze was cast into guns, bells and statues.

With advances in electrical engineering copper has become the principal material in the manufacture of conductors and other current-carrying parts. Today, about half the copper produced goes into electrical engineering.

The high thermal conductivity of copper has spurred its use in heaters, coolers, automobile radiators and other heat-exchanging devices.

A remarkable feature of copper is its ability to make a large number of diverse alloys. The most numerous group is represented by brasses which include tombac (90 per cent Cu and 10 per cent Zn), Muntz-metal (60 per cent Cu , 30 per cent Zn , tin and lead), to mention only two. Brasses are superior to copper both in mechanical properties and workability. They are cheaper to make than pure copper, as they use the cheaper zinc. Brasses have found a broad field of application in general and chemical engineering.

Bronzes are alloys of copper and tin, the latter running up to 20 per cent. Though harder than copper, bronzes machine and cast well. Owing to high resistance to corrosion, bronzes are made into valves and fittings for water and gas pipelines and chemical apparatus. Their low coefficient of friction and wear resistance are utilised in bearings, worms and worm wheels, gears, etc.

Tin, however, is more expensive than copper. To make bronzes cheaper and to save tin, low-tin and tinless bronzes have been developed. The former include bronzes OQ and OQC in which part

of the tin is replaced by zinc and lead, and the latter are represented by bronze БАЖМ (containing aluminium, iron and manganese).

Alloys of copper and nickel are used on a limited scale. The most important among them are German silver (80 per cent Cu and 20 per cent Ni) and Monel metal (68 per cent Ni, 28 per cent Cu, manganese and iron). Monel metal is highly resistive to corrosion, has high mechanical properties and is machined readily. Therefore, it is widely used in precision engineering, for surgical instruments, high-performance chemical apparatus and coinage.

Copper salts, mainly blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), find uses in the chemical, tanning and fur industries, and also in dye-stuffs and rayons.

50. Sources of Copper

In general, copper ores rarely contain more than 1 or 2 per cent copper. Deposits containing less than 0.5 per cent copper are not worked at present. Table 11 presents the copper minerals occurring in copper ores most often.

Table 11

The Most Important Copper Minerals

Mineral	Chemical formula	Copper content, per cent
Chalcopyrite	CuFeS_2	34.6
Bornite	$5\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$	55.6
Chalcocite	Cu_2S	79.9
Covellite	CuS	68.5
Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	57.4
Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	55.1
Cuprite	Cu_2O	88.8
Tenorite (melaconite)	CuO	79.9
Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$	36.2
Native copper	Cu	up to 99.9
Carrotite	CuCo_2S_4	21.0
Heterogenite	$2\text{Co}_2\text{O}_3 \cdot \text{CuO} \cdot n\text{H}_2\text{O}$	—

The ores are classified in three groups: sulphide, oxidised and native copper.

The sulphide ores may occur either as massive bodies mainly consisting of copper and iron sulphides, or in small particles disseminated through monzonitic igneous rock called "porphyry". The massive ore bodies contain more sulphur and copper.

The oxidised ores are mainly of the disseminated type, and the greater part of iron in them is present in the form of oxides, carbonates and silicates.

There may also be mixed ores containing both oxidised ores and copper sulphides.

Copper ores are usually complex, the other minerals in them being zinc, lead, nickel, molybdenum, gold, and silver as well as sulphur, selenium, tellurium, thallium, cobalt, etc.

Copper concentrates produced by flotation assay 11 to 35 per cent copper. Selective flotation of complex ores also produces lead, zinc or nickel concentrates for the manufacture of the respective metals. Copper-molybdenum ores are treated to recover both copper and molybdenum concentrates, and copper-cobalt ores are additionally treated for cobalt concentrates.

Rich copper concentrates are difficult to obtain because of mineral intergrowth. The usual practice is either to float the copper ore for a copper concentrate and a pyrite tailing, or to obtain a copper-pyrite concentrate which is then separated by refloatation. Up to 85 per cent copper is removed from pyrite ores into the copper concentrate. The pyrite tailing, which contains 40 to 50 per cent sulphur, is utilised in the production of sulphuric acid. In the case of complex ores, such as copper-zinc ores, flotation recovers 80-90 per cent copper and 65-70 per cent zinc. The composition of copper concentrates is given in Table 12.

Table 12

Composition of Copper Concentrates

Original ore	Composition, per cent						
	Cu	Zn	S	Fe	SiO ₂	Al ₂ O ₃	CaO
Pyrite ore	11-20	4-7	35-43	32-37	3-5	3-7	0.5-2
Copper-zinc ore	11-15	2-4	30-35	25-30	3-5	3-7	0.5-2
Disseminated ore	20-25	—	30	25-27	5-10	5-8	0.5-2
Porphyry ore	28-35	—	15-20	16-20	20-29	5-8	1-2

A proportion of copper is obtained from scrap and wastes collected and classed accordingly (secondary copper). Brass and bronze scrap is recovered separately, with suitable additions to control the final analysis. Lean and off-grade wastes are treated for the recovery of pure copper. Off-grade wastes are those which cannot be sorted out accurately; they usually contain 8 to 75 per cent copper.

51. Production of Copper from Ores and Concentrates

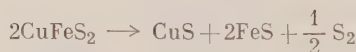
Copper may be extracted from its ores and concentrates either by smelting or by leaching, about nine-tenths being obtained by smelting (the pyrometallurgical method).

The Pyrometallurgical Method (Smelting). Concentration does not change the composition of the minerals treated, the only difference between the original ore and the resultant concentrate being a quantitative one. For this reason, the same physicochemical principles underlie copper smelting from ores and concentrates.

When a charge of sulphide ore or concentrate is molten, the bath separates into two layers: the molten sulphides and the molten oxides. The stratification is due to the difference in specific gravity and the fact that molten sulphides and oxides are nearly insoluble in each other.

The sulphides form the matte, and the oxides produce the slag. The slag floats on the matte, as the specific gravity of mattes is about 5 and that of slags about 3.

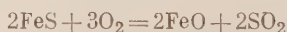
Before they are fluidised, the copper and iron minerals of the charge decompose into simple sulphides and sulphur vapour:



Simple iron and copper sulphides are stable at elevated temperatures. Therefore, irrespective of the mineral form of iron and copper sulphides, the molten matte will be an alloy of Cu_2S and FeS .

In smelting, the gangue (SiO_2 , CaO , Al_2O_3) passes into the slag which can be easily separated from the matte and removed from the furnace, thereby concentrating the copper in the matte.

Some of the iron in the matte can be slagged by blowing it with air:

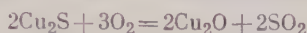


The charge always carries some quartz with which the ferrous oxide forms a silicate



and becomes a constituent of the slag.

At the same time, some of the copper sulphide may be oxidised:



For all practical purposes, however, only the FeS is oxidised, as the Cu_2O reacts with iron sulphide to be converted back to copper sulphide:



According to Volsky (U.S.S.R.), the free energy change of this reaction in the range 900-1300°C varies between -30.1 and -35.8 kcal. The equilibrium constant is:

$$K_{eq} = \frac{a_{(\text{Cu}_2\text{O})} \cdot a_{[\text{FeS}]}}{a_{[\text{Cu}_2\text{S}]} \cdot a_{(\text{FeO})}}$$

and can be found approximately by the equation:

$$\ln K_{eq} = -\Delta G/RT$$

For the extreme temperatures given above, the values of K_{eq} will respectively be about $10^{-1.6}$ and $10^{-4.98}$. Assuming that $a_{[\text{FeS}]}$ approximates $a_{(\text{FeO})}$, which agrees well with practice, the ratio of the activities of Cu_2S in the matte and Cu_2O in the slag will show that the activity of the latter is vanishingly small, and the reaction under discussion will proceed to completion.

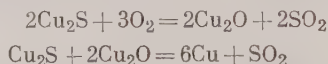
The conversion of the cuprous oxide by iron sulphide into a sulphide proceeds rapidly and fully. As a result of this reaction, which may be considered the key reaction of the pyrometallurgical method, the copper of the ore is concentrated in the matte, and the iron is slagged.

The extent to which the iron sulphide is oxidised is indicated by the ratio of the oxidised sulphur to the original sulphur in the ore. The more the sulphur is oxidised, the richer is the matte in copper.

Some of the sulphur can be oxidised prior to smelting by roasting, which is usually employed for ores high in sulphur. If roasting or smelting oxidised all of the sulphur, the iron would be completely withdrawn into the slag, and what is known as blister copper (79.9 per cent copper) would be obtained. It would, however, be wasteful of the metal to try and obtain blister copper directly by fusion, as with more copper in the matte mechanical losses grow due to the drops of molten metal caught in the slag. The actual procedure is therefore to obtain a matte relatively low in copper and, consequently, a slag with less copper, which may go to waste. The iron left in such a matte is eliminated in a converter, resembling the Bessemer vessel. First, the iron sulphides are oxidised selectively, then the ferrous oxide is fluxed by adding some quartz into the converter. After all iron has been removed, the resultant melt

is the white matte. The slag is tapped and retreated for the recovery of its copper.

To obtain metallic copper from the white matte, the air blast is continued; the copper sulphide is oxidised to cuprous oxide which immediately reacts with the sulphide residue:



After the smelting operation the blister copper remains. The blister copper is then refined either in a reverberatory furnace or electrolytically.

A general scheme for treating copper ores by the pyrometallurgical method is shown in Fig. 68. Referring to it, it is possible to melt the ore directly, or to melt the concentrate with or without previous roasting. In the case of the sulphide ores and concentrates, part of the sulphur has to be oxidised and eliminated with gases in order that the copper can be separated from the iron. The mixed ores carry less sulphur than the sulphide ores; therefore, they can be treated by the same method, except that less sulphur may be removed. The oxidised ores may be smelted in a mixture with the sulphides. Thus, smelting to produce the matte is good for any ore, provided it carries enough sulphur to produce a matte.

Flotation copper concentrates are in powder form. Therefore, they are smelted in reverberatory or electric furnaces capable of handling a fine-size charge, while copper ores, usually in coarse lumps, are smelted in a blast furnace. Sometimes, copper concentrates are briquetted or sintered, in which case they may be smelted in a blast furnace. Rich ore fines are charged together with concentrates for smelting in reverberatory or electric furnaces.

Going back to the matte, it should be noted that the aggregate content of Cu_2S and FeS in it seldom exceeds 80 to 90 per cent, the balance being sulphides of zinc, lead, nickel and other impurities, as well as oxides of iron, silicon, aluminium, and calcium, i.e., constituents of the slag partly soluble in the matte. Iron oxides are more soluble in the matte than other oxides. The molten matte is a good collector of the precious metals as they dissolve poorly in the slag.

The maximum copper content in the matte is 79.9 per cent. Mattes carrying less than 10 per cent Cu are avoided, as they are difficult and expensive to refine. In most cases, a typical matte will contain 20 to 40 per cent copper.

Sulphur runs 36.4 per cent in iron sulphides and 20 per cent in copper sulphides. Naturally, the sulphur content in the matte must be within these limits. In most cases it is 24 to 26 per cent. Accordingly, Mostovich (U.S.S.R.) has suggested an empirical

rule by which the sulphur content in all metallurgical calculations should be assumed equal to 25 per cent.

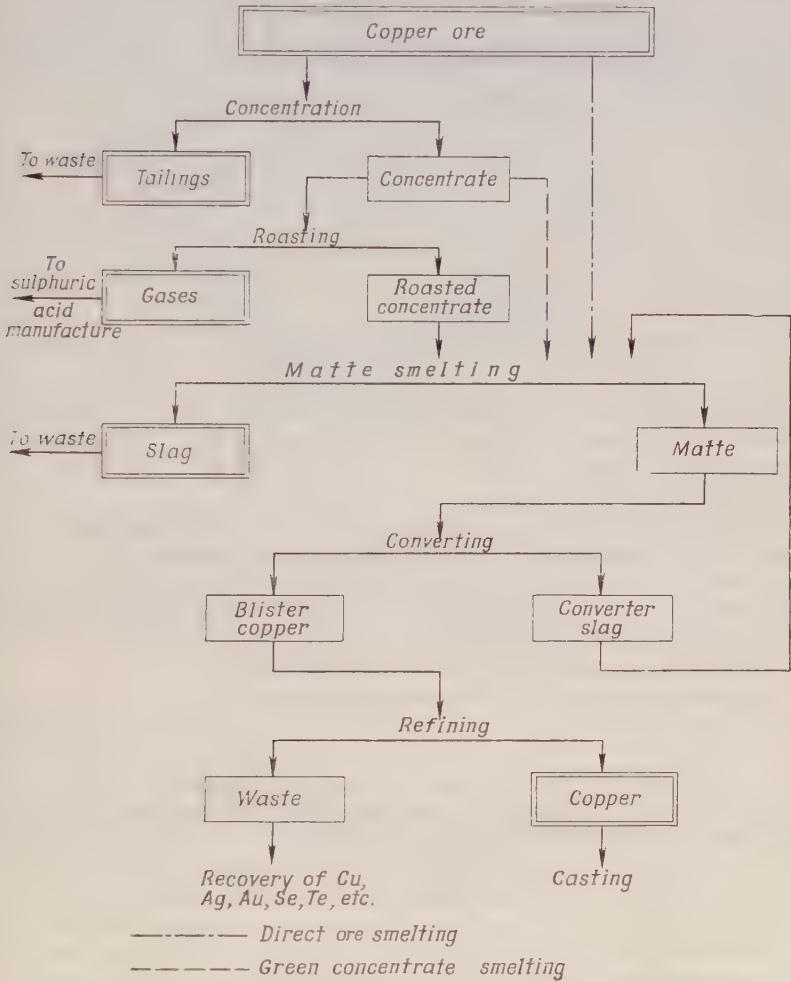


Fig. 68. General flow-sheet for copper smelting

In his studies of mattes, Mostovich has established that they may contain as much as 7 per cent oxygen as a constituent of the ferrites dissolved in the matte ($MO \cdot Fe_2O_3$), increasing with decreasing copper in the matte. Table 13 presents the data of his findings, as verified by Avetisyan.

Table 13

Composition of the Matte
(after Avetisyan)

Composition, per cent				
Cu	Fe _{tot}	Fe ₃ O ₄	O	S
10	57.66	23.6	6.54	25.8
20	49.32	19.4	5.38	25.3
30	41.00	15.2	4.20	24.8
40	32.68	10.9	3.02	24.3
50	24.80	7.7	1.90	23.3
60	16.20	2.5	0.70	23.1

The melting point and specific gravity of the matte, both vital properties, depend on its composition. Mattes rich in copper are heavier and melt at a higher point than mattes low in copper. Commercial mattes melt at 900 to 1150°C and have a specific gravity of 4.6 to 5.2.

The slags of copper smelting are similar in composition and properties to the slags of other non-ferrous metals. In all cases they are high in FeO, in which respect they differ from blast-furnace slags which are relatively low in ferrous oxide. This is because before the mineral metal can be extracted from its ore, the iron has to be separated and withdrawn into the slag.

Usually, the copper-smelting slag either goes to waste or is utilised as a by-product. Yet, it greatly affects the economy of copper smelting, for it carries off valuable metals and some fuel is burned to melt the slag. The losses increase with increasing metal content of the slag and the quantity of slag produced per unit weight of metal or matte.

The slag yield varies with the charge composition and the quantity of flux added, while the metal content of the slag depends on the properties of the slag and the conditions under which a given heat is run.

The metal losses with the slag are customarily classed into three groups:

(1) Chemical losses due to the fact that the principal reaction of a given smelting process fails to proceed to completion, and the oxide of the metal remains partly dissolved in the slag. In the case of copper, it is mainly lost as Cu₂O not completely sulphurised by the iron sulphide. Experience and the above calculations show that these losses are negligible.

(2) Physical losses due to the dissolution of the metal or matte in the slag and the formation of colloidal solutions. The solubility of copper sulphide in slags varies with temperature, the maximum being 0.2 to 0.3 per cent.

(3) Mechanical losses due to the incomplete separation of molten metal or matte from molten slag because of the insignificant difference in their specific gravities, short dwell, or the high viscosity

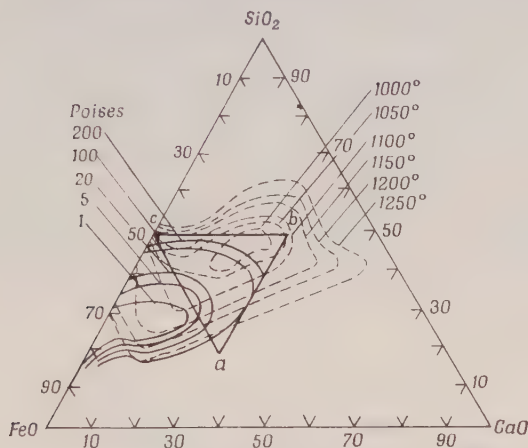


Fig. 69. Three-component diagram, FeO-CaO-SiO₂, showing fusibility and viscosity of slags (after Loskutov) and composition of real slags (small triangle) (after Gudima)

of the slag. Usually, this type of loss accounts for the better part of total loss, including copper smelting.

The slags of copper smelting are closest in composition to the slags of nickel, lead and tin smelting and carry a total of up to 90 per cent SiO₂, FeO and CaO. They also contain up to 15 per cent Al₂O₃ and, sometimes, as much as 25 per cent Fe₃O₄ (converter slags), as well as oxides of magnesium, barium, sodium and some other metals.

A slag should not be too refractory, as this adds to the costs of smelting due to the increased fuel consumption and the wear of the lining. In copper smelting, the slag usually melts at 1100-1250°C.

Some of the constituents of the slag have very high melting points. SiO₂, for example, melts at 1713°C, FeO at 1377°C, and CaO at 2570°C. Their mixtures melt at much lower temperatures.

The selection of a good slag can be greatly facilitated by the chart given in Fig. 69. In this chart, the melting point of a slag is related to its viscosity and composition. As the chart takes into

account only three main components of slags, practical slags, such as used in smelting practice, somewhat differ. According to Gudima (U.S.S.R.), all practical slags may be placed within the triangle *abc*. With any slag, the primary consideration is that it should use the cheapest fluxes and in the smallest quantities. As a rule, some increase in the content of FeO, MnO, CaO and BaO reduces the viscosity of slags, while SiO₂, Al₂O₃ and Fe₃O₄ act often to the opposite. In some cases, materials nearly insoluble in a slag raise its viscosity by forming solid particles suspended in the molten material.

Apart from its melting point, the surface tension of the slag at the interface between the matte (or metal) and gases is also a very essential property. If the slag fails to wet the metal or matte sufficiently, their droplets may be lifted to the surface by gas bubbles much as mineral particles are in the flotation process. The surface tension in the system FeO-SiO₂-CaO has been investigated by Vanyukov (U.S.S.R.). His chart is given in Fig. 70.

In solidified slags, the oxides form chemical compounds, mainly silicates of the type $xMO \cdot ySiO_2$. In the past, the prevailing theory has been that in molten slags these compounds partly dissociate into free oxides:



Various silicates dissociate to a different degree, the governing factors being their affinity, temperature and concentration in molten slag. The oxides which form more durable silicates will destroy weaker silicates:



A comparison of their stability may be obtained by relating their free-energy changes of formation from oxides and silica to gram-mole of SiO₂ (Fig. 74).

According to the hypothesis recently advanced by Vanyukov and followed up by many investigators, including Yesin (U.S.S.R.), the silicates in a slag dissociate like salts:



That the molten slags have ion conductivity and may be electrolysed with the deposition of the metal on the cathode has been proved by experiments.

According to the ion theory of slags, the silicon in them is present as the SiO₄⁴⁻ ions and other more complex anions. Metal oxides dissociate into the ions of metals and oxygen:



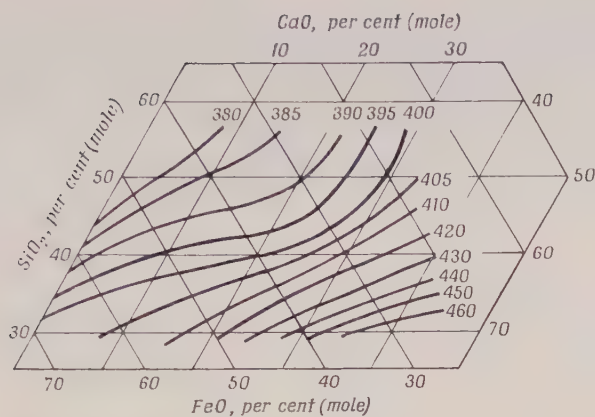


Fig. 70. Three-component diagram, FeO-CaO-SiO_2 , showing surface tension as a function of composition (after Vanyukov)

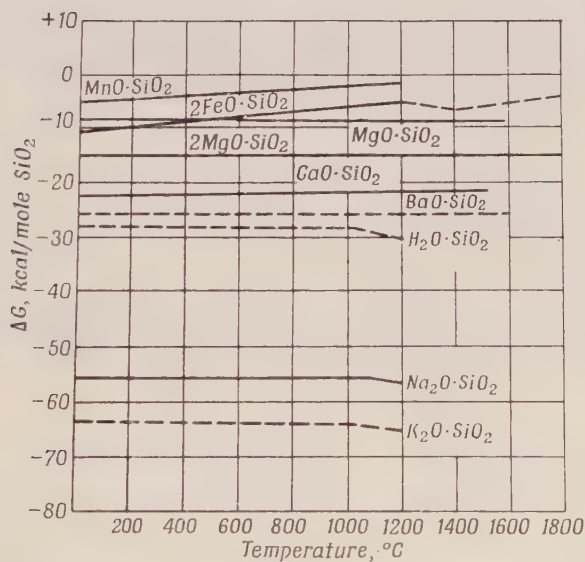


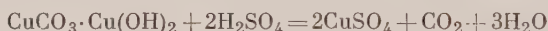
Fig. 71. Standard free energies of formation for some silicates (per gram-mole SiO_2)

Slags are microheterogeneous, i.e., the ions in them are distributed non-uniformly: those of oxygen concentrate primarily around small-radius cations, while the silicon-bearing ions around the larger cations. The radius of the Ca^{2+} ion (1.06 Å) is greater than that of the Fe^{2+} ion (0.83 Å). For this reason, when some calcium oxide is added to the slag the number of silica anions around the iron ions decreases, and the activity of the ferrous oxide rises in proportion.

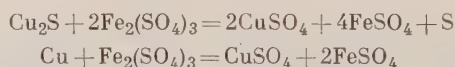
Hydrometallurgical Methods. Copper is extracted by leaching from lean, oxidised and mixed ores which are difficult to concentrate. Often these ores carry native copper. The main drawback of most hydrometallurgical methods is the loss of precious metals.

The usual reagents are sulphuric acid and ammonium salts. Accordingly, there are sulphuric-acid and ammonia processes.

Sulphuric acid easily dissolves oxidised copper minerals, such as malachite:

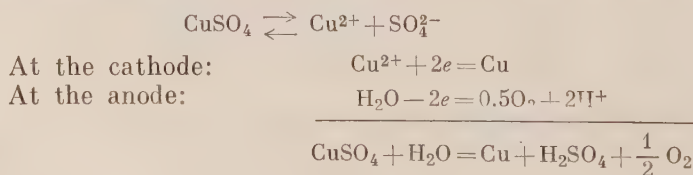


On the other hand, sulphuric acid does not practically act on sulphide ores and native copper. From them the copper may be leached by means of the sulphate of iron oxide:



With chalcopyrite and boronite these reactions proceed slowly and never reach completion.

After the insoluble material is filtered off, the remaining solution is electrolysed in cells using insoluble lead anodes. Metallic copper is deposited at the cathodes, while the water molecules are decomposed at the anode to produce oxygen, and sulphuric acid is regenerated in the solution, which goes to leach copper ore again. The electrolysis of copper may be pictured as follows:



Solutions carrying too much ferrous sulphate are not attractive for electrolysis for the reason that the Fe^{3+} ions are deposited at the cathode together with copper, thereby involving waste of electricity. In such cases, it will pay to first remove some of the

iron from the solution either by reducing it with sulphurous gas or with cement copper. Instead of electrolysis, copper may be precipitated from solutions, especially from lean ones, by means of iron scrap (cementation):



Fig. 72 shows a simplified flow-sheet for the extraction of copper by the sulphuric-acid process.

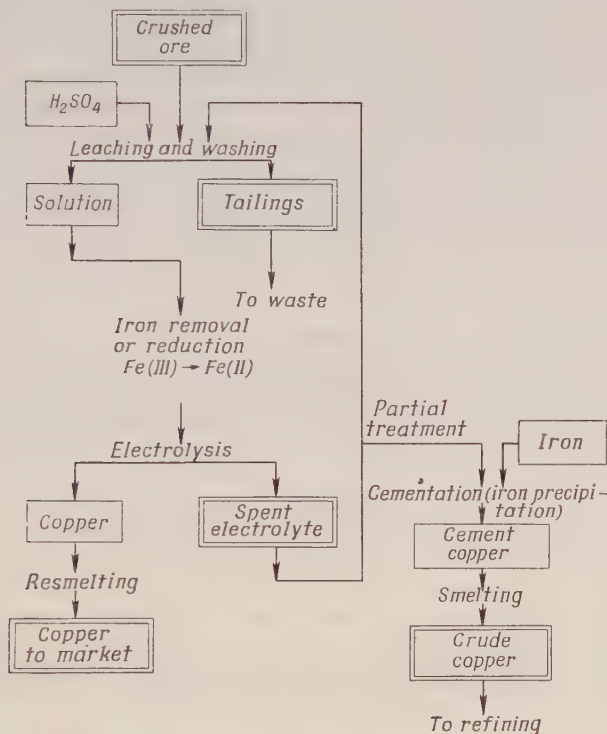


Fig. 72. Flow-sheet for the sulphuric-acid process of copper extraction

The use of ammonia and ammonium carbonate is more attractive than of sulphuric acid for ores containing carbonates and other minerals which react with sulphuric acid. Oxidised copper minerals react with ammonium compounds to form cuprous-ammonium carbonate:



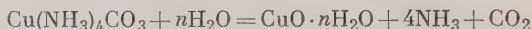
The cuprous-ammonium carbonate can dissolve copper:



In the presence of air, the cuprous compound is rapidly oxidised to cupric and again becomes an active leaching agent:



When the solution containing cuprous- or cupric-ammonium carbonate is blown with steam, both the ammonia and carbonic acid are distilled off and condensed, while the copper is precipitated as $\text{CuO} \cdot n\text{H}_2\text{O}$:



The copper residue is filtered out and reduced to metallic form by smelting it with coal, while the gases NH_3 and CO_2 are absorbed by water and are returned to the process.

Special promise for lean oxidised and especially mixed ores is held out by the combination (flotation-leaching) process developed by Mostovich. By this process, mixed ores are leached with sulphuric acid; the copper that passes into solution from the oxidised minerals directly in the feed is cemented by sponge iron; then the copper sulphides and cement copper together are floated to obtain a copper concentrate. This concentrate usually contains precious metals which associate with copper.

Hydrometallurgical methods are employed more seldom than pyrometallurgical. Yet, as much as 20 per cent of all primary copper is produced hydrometallurgically.

52. Matte Smelting from Ores

If a sufficiently rich matte is to be obtained from copper ores usually carrying 1 to 2 per cent copper, nearly all iron has to be slagged off. This calls for a high level of desulphurisation which is done in a copper-smelting furnace. There are three processes of smelting: (1) the pyritic process; (2) the partial or semi-pyritic process; and (3) the copper-sulphur process.

Pyritic and Partial Pyritic Smelting. A copper-smelting furnace is a tall shaft filled with a burden of coarse ore, flux and coke. The air blast necessary to oxidise the sulphides and to sustain the combustion of the fuel is blown through the tuyeres in the lower portion of the shaft.

The slag which forms in copper smelting carries some ferrous oxide. Therefore, it would scour aluminosilicate and quartz refractories if they were used as the lining. Magnesite would stand its action, but magnesite bricks are weak mechanically and cannot stand up to heat. Instead, the walls of copper-smelting furnaces are made up of iron water jackets welded from boiler plate (Fig. 73). Their

surface facing the charge is usually covered by a crust of chilled material which remains permanently. The bottom plate of the furnace is a rectangular cast-iron slab supported by steel columns or by jacks on a foundation.

The side jackets are given a slope towards each other to form a bosh, the upper and end jackets being vertical. The end jackets are set up in pairs and have the shape of a trapezoid.

The lower side jackets are pierced for tuyere openings. The tuyere thimbles are made fast to the water jackets and connected to the air main, or the bustle pipe.

Cooling water is fed to each of the jackets from a common water line. When it leaves the jackets, the water is 70 to 80°C hot. It is discharged into launders from which it passes through a cooling tower and is again re-cycled through the cooling system. This arrangement excludes scale formation in the jackets.

The charge is fed into the furnace from a platform located at and along the top edge of the side jackets.

The matte and slag are run off jointly through an opening in what is known as the breast jacket—a copper slab with a flat cooling coil embedded in it. The breast jacket is located in the side of the furnace. The slag spout conveying the molten products to the settler (Fig. 74) is fastened to the breast jacket so that its discharge end is above the opening in the jacket. As the molten material from the furnace rises in the spout, a sort of hydraulic seal is formed to trap the blast.

The settler is usually oval in plan, and its axis is at right angles to the long axis of the furnace. It consists of an iron-plate shell lined with chrome-magnesite or talc stone. The roof of the settler is formed by the chilling of the slag on which old water jackets are placed. In the settler the matte and slag separate. The slag flows down an overflow at the opposite end of the settler. The matte is withdrawn through tap holes located on the side close to the bottom.

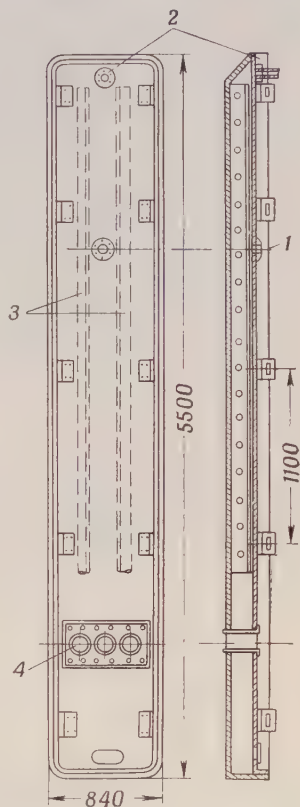


Fig. 73. Water jacket of a copper blast furnace:

1—water in; 2—water out;
3—stiffeners; 4—tuyere openings

Above the charging floor is the firebrick superstructure which has charging ports with hinged doors and a firebrick hood for the removal of the furnace gases. In hot-run furnaces the entire structure is of steel and sometimes water-jacketed.

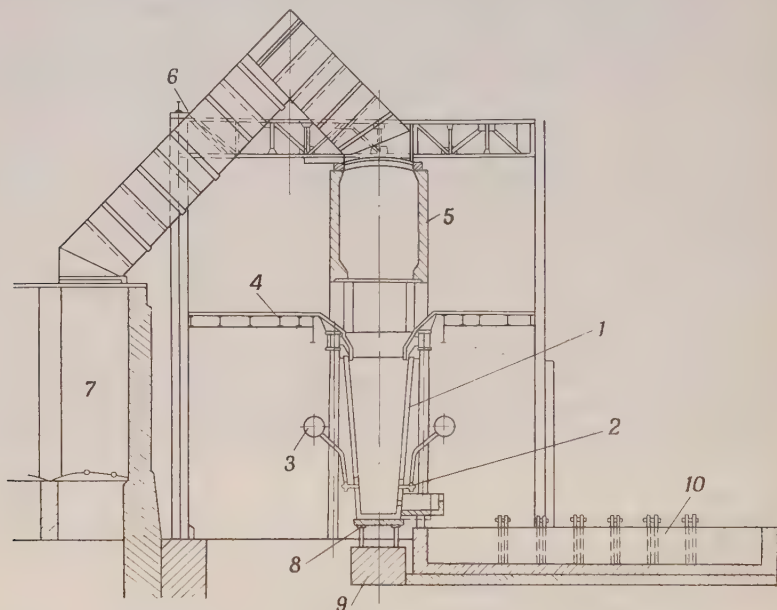


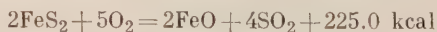
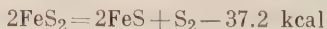
Fig. 74. Copper-ore blast furnace:

1—water jackets; 2—tuyeres; 3—bustle pipe; 4—charging floor; 5—hood; 6—gas flue; 7—settling chamber; 8—hearth bottom; 9—foundation; 10—settler

On leaving the hood, the gases pass through a downcomer and into a settling chamber to get rid of the coarse particles of dust and then go into the stack.

What singles out this type of smelting is that the bulk of the heat required to conduct the operation comes from the oxidation of the pyrite and other constituents of the ore, and from the formation of ferrous silicates and calcium oxide.

The formation of ferrosilicate from pyrite may be described as follows:



Where the ore carries at least 37 per cent sulphur (69.4 per cent FeS_2), smelting will proceed without any extraneous fuel.

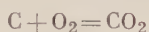
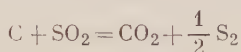
Under normal conditions, smelting without any extraneous fuel is rather unstable, and so at least 2 per cent coke is added to the burden. Yet, the bulk of heat comes from the oxidation of the pyrite and the process is called pyritic.

As more coke is added to the charge, the progress of smelting becomes steadier and more controllable. When over 6 per cent coke is added to the charge, the process is termed partial pyritic.

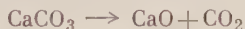
In the U.S.S.R. the theory and thermochemistry of the two processes—pyritic and partial pyritic—have been investigated by Baikov and Mostovich.

In copper-smelting blast furnaces, the pyrite and coke burn most intensively at the tuyeres where the temperature may be as high as 1400-1500°C. Rising through the burden which may be 3 to 5 metres deep, the hot gases leave the top to enter the settling chamber after which they may be treated for the recovery of sulphur dioxide or discharged into the atmosphere through a stack. At the top, the temperature of the gases is 350-550°C.

As the charge descends in the furnace against the ascending column of hot gases, its temperature gradually rises, and the higher sulphides, such as pyrite, chalcopyrite, covellite and bornite, are completely dissociated. The free sulphur is carried off as heavy fumes of elemental sulphur, being oxidised to SO_2 and SO_3 on their way out. Then the sulphides are ignited, the rate of burning increasing with temperature. In the shaft, the carbon of the coke is oxidised by the sulphur dioxide, while in the hearth this is accomplished by the oxygen of the air blast:



The limestone is decomposed into CaO and CO_2 :

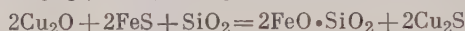
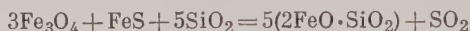
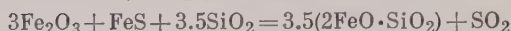


At about 1000°C the sulphides begin to be melted out of the ore lumps, leaving behind a porous structure of quartz and oxides of iron, calcium, magnesium and aluminium.

The lowest-melting oxides in the system SiO_2 - CaO - FeO melt at 1100°C. Dripping down, they gradually dissolve the other oxides of the earthy material.

The porous mass of hard oxides formed by the melting out of low-melting constituents plays a noticeable part in melting. In its pores, the molten sulphides run into the uprising current of hot oxygen-bearing gases. The large contact area and the high temperature serve to speed up the most important reactions of the

process:



The fused mixture of sulphides and silicates flows through the spout to the settler.

Anywhere from 50 to 95 per cent sulphur burns out in the blast furnace, varying with the composition of ores. Indeed, a rich matte may be obtained even from lean ores.

The coke, when added in small quantities, burns in the top layers of the burden mainly due to SO_2 , without reaching the tuyere zone (pyritic smelting). Where more coke is added, it burns also with the oxygen of the air blast entering the furnace through the tuyeres, and less sulphur is burned out in the course of smelting. The burning of the coke in the tuyere zone is responsible for a more stable thermal cycle in the focus of combustion (semi-pyritic working).

The blast-furnace slags mainly contain SiO_2 , FeO and CaO (Table 14). The proportion of these constituents is closely related

Table 14

Approximate Composition of Copper Blast-furnace Slags

Process	Composition, per cent							
	Cu	SiO_2	FeO	CaO	Al_2O_3	MgO	S	ZnO
Pyritic	0.18	32.6	49.9	8.2	1.5	3.5	1.7	1.9
Ditto	0.15	32.5	52.2	4.8	7.2	—	0.9	—
Partial pyritic	0.16	30.0	34.6	12.0	11.0	—	—	—
Ditto	0.16	39.9	22.4	26.8	6.4	—	0.5	1.4
Copper-sulphur	0.20	33.6	52.8	6.0	1.6	—	2.9	0.6
Ditto	0.18	32.4	55.2	6.0	—	—	—	Traces

to the melting conditions, especially the amount of coke added. Where coke addition is small, and the ore mainly consists of pyrite, quartz is usually employed as flux. Additions of limestone and other materials to the charge should be kept to a minimum, or else the heat supplied by the combustion of the pyrite may prove insufficient to melt the charge.

As often as not the slags of pyritic smelting are very viscous due to the presence of dissolved and suspended magnetite. The

latter may be formed where there is no direct contact between the quartz and the iron sulphide, and the latter is oxidised to Fe_3O_4 .

In partial pyritic smelting, the additional heat input makes it possible to vary the slag composition more freely, above all to reduce the content of FeO , and consequently to lower its specific gravity. The content of SiO_2 in such slags usually is 40 to 45 per cent and of calcium oxide 12-27 per cent.

The minimum size of ore, flux and coke for blast furnaces should be 20-15 mm, the prevailing size being 70 mm in diameter. The proportion of smalls less than 20 mm in diameter should not exceed 10 per cent, or the passage of the gases through the burden may be handicapped.

The part of the charge consisting of ore, fluxes and flue dust is called the burden, and the part consisting of coke is called the blank. The two parts are charged into a furnace in turn.

The molten matte is withdrawn from the settler at regular intervals as it accumulates there, while the slag continuously flows out of the settler into slag ladles which take it to the dump while hot. Sometimes, the slag may be granulated.

For the blast to be maintained at the proper rate, the tuyeres should be cleaned at regular intervals, the level of the stockline kept constant, and the lump size of the charge materials controlled.

With time, incrustations build up on the inside surface of the furnace, sometimes closing it. Their build-up may be due to a variety of factors, the principal one being the non-uniform distribution of the gas stream across the horizontal cross-sectional area of the stack and the non-uniform heating of the charge.

Another cause may be the upset stoichiometric relationship between the quartz, iron sulphide and oxygen in the melting zone when little coke is added to the charge. In such cases, an excess of quartz or lack of air may result in a lack of FeO necessary to slag the quartz, and so silicate incrustations build up. Where an excess of air or a lack of SiO_2 is present, the FeO is often oxidised to Fe_3O_4 , and high-melting magnetite incrustations are formed.

There always is some difficulty in removing the incrustations for which reason even clean pyrite ores are often smelted with an increased addition of coke.

Losses to dust in blast-furnace smelting may be as high as 5 per cent of the charge (by weight), increasing with increasing proportion of smalls in the burden. Dust settles in the flues and the dust catcher, while the smaller dust specks are trapped by electrical precipitation filters. The composition of the dust is usually very close to that of the ore. In most cases, the dust is smelted in reverberatory furnaces in company with copper concentrates. In some cases, it is briquetted or sintered for smelting in blast furnaces.

In blast-furnace smelting 78 to 85 per cent copper is withdrawn from the ore into the matte, which is a low figure because too much slag is produced per unit weight of the matte. The daily output of furnaces is assessed in terms of metal weight per square metre of furnace area at the tuyeres. Usually, it ranges between 50 and 120 tons/sq m, being smaller for working with little coke. Where 2 or 3 per cent coke is added to the charge, the daily output will not exceed 60 tons/sq m.

Present-day blast furnaces use mechanical charging and matte and slag handling. Work is well ahead on applying automatic control to them, especially that of blast pressure as a function of the burden depth and the temperature of the flue gases.

Blast-furnace mattes usually assay 15 to 25 per cent copper, depending on the composition of the ore and the degree of desulphurisation. With rich ores, it is possible to obtain a matte containing 45-50 per cent copper. In the slag, the copper content ranges between 0.15 and 0.45 per cent, about 0.3 per cent being the most usual case.

A blast furnace can remain in operation from 4 to 18 months, the average being 10-12 months.

The Copper-sulphur Process. In this process both a matte and elemental sulphur are obtained from the ore simultaneously.

Furnaces for copper-sulphur smelting are taller than ordinary blast furnaces and have water jackets at the bottom only. The top of the stack is of firebrick and encased in an iron shell. The stack is topped by an arch. The surface of the water jackets facing the charge is lined with a layer a quarter to a half the thickness of fireclay brick. So, high temperature and a reducing atmosphere can be maintained at the top of the stack, and air leakage eliminated between the water jackets and through the brickwork joints.

The burden is charged in a way similar to the one used in pig-iron blast-furnace practice.

Flue gases are withdrawn through an opening in the side of the superstructure near the arch (Fig. 75).

The tap hole for matte and slag is higher above the hearth bottom than in ordinary copper-blast furnaces, and the bath of matte and slag up to 1 metre deep may be maintained in the crucible.

The copper-sulphur process is characterised by the same reactions of sulphide combustion, oxide formation, interaction between cuprous oxide and iron sulphide, and the formation of ferrous silicates and calcium oxides.

In the tuyere zone, the carbon of the coke is burned to CO_2 , and some of the sulphur brought in with the sulphides is burned out.

The gases carrying SO_2 , CO_2 , nitrogen and an excess of oxygen rise through the charge, the excess of oxygen being gradually spent to oxidise the sulphides and to sustain the combustion of the carbon. The carbon dioxide interacts with the carbon to be partly turned

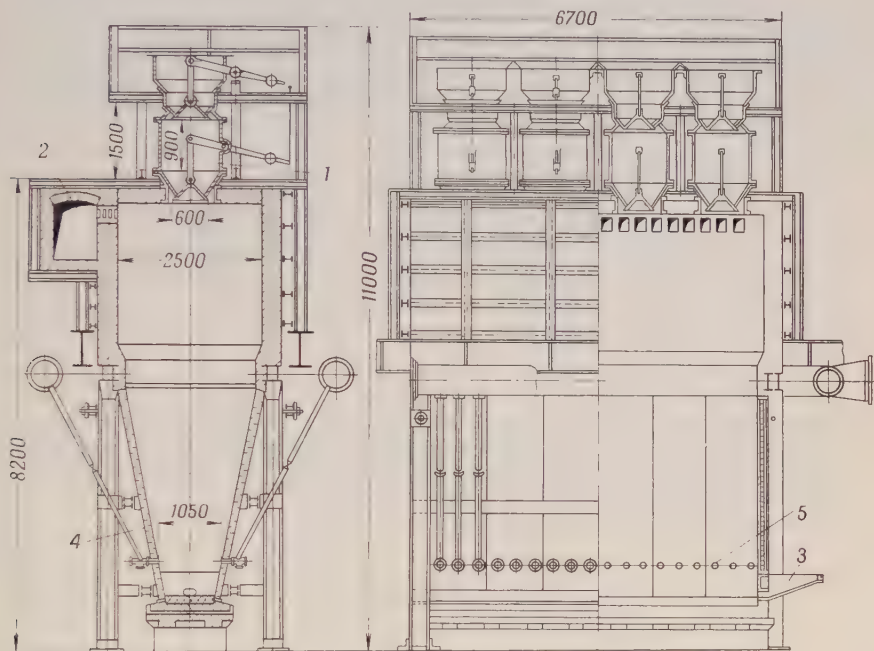
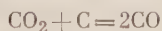


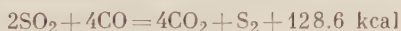
Fig. 75. Blast furnace for the copper-sulphur process:

1—charging arrangement; 2—gas off-take; 3—launder; 4—water jacket; 5—tuyeres

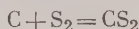
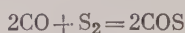
to CO ; the water brought in by the blast and burden is either decomposed or interacts with the sulphides to form hydrogen sulphide:



In other words, the gas changes analysis as it ascends: the content of CO_2 , O_2 and H_2O in it is decreased due to the formation of carbon monoxide, sulphur dioxide and hydrogen sulphide. Higher up the furnace, some of the sulphur dioxide is reduced to sulphur:



The further interaction of the sulphur vapours and the carbon monoxide and carbon produces COS and CS₂:



In the top levels of the burden, the sulphur vapours produced by the dissociation of pyrite and other higher sulphides are also added to the furnace gas.

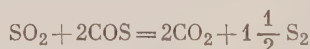
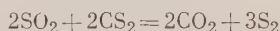
The top gases have the following approximate analysis (grams/cu m):

S ₂	SO ₂ + H ₂ S	COS	CS ₂	Dust
200-220	30-35	4.4-5.0	8.2-16	15-50

The gases should leave the furnace at a relatively high temperature (430-450°C) in order that they may be cleaned of dust before the sulphur vapours begin to condensate. The gases are taken to a gas receiver where they are mixed to obtain a uniform composition. The bulk of dust settles in the gas receiver and gas flues, while the final dust removal is effected in electrical precipitators.

The cleaned gas is fed to contact chambers filled with a porous catalyst consisting of alumina cement and aluminium hydroxide.

In the presence of the catalyst, the constituents of the gas mixture maintained at about 450°C react with one another to produce vapours of elemental sulphur:



From the contact chambers, the gases are passed through water-tube boilers where the sulphur is deposited on the tubes and settles in a receiver; the heat given up by the vapours is used to generate low-pressure steam.

In condensing, the gases cool down to about 120°C. At that temperature the gases are fed into a drip cooler where their flow rises towards a stream of molten sulphur flowing down the checkerwork, and so the fine drops of sulphur suspended in the gases are recovered.

Only some of the sulphur is recovered in the contact chamber and the drip tower. Therefore, the gas is reheated to 450°C and is passed into a second line of similar plant.

The remaining waste gases which still carry some quantity of H₂S and fine sulphur particles are treated for safety in checker towers sprinkled with milk of lime.

Copper-sulphur mattes contain 5-10 per cent copper. To facilitate subsequent treatment, they are first resmelted in ordinary blast

furnaces in a way similar to semi-pyritic smelting: the iron of the matte is oxidised and slagged, and the copper content is thus raised to 25-40 per cent. The resultant slag carrying 0.4 to 0.8 per cent Cu is recycled.

As compared with pyritic and semi-pyritic smelting, the copper-sulphur process is less efficient and burns more coke. The daily output does not usually exceed 35-40 tons per sq m of area at the tuyeres, while the coke consumption is as high as 10-12 per cent of the charge weight. The lower quality of the matte and the increased coke consumption in the case of the copper-sulphur process are compensated by the by-product sulphur. The breakdown of the products involved in the process (in per cent) is approximately as follows:

Elemental sulphur recovered	68
Matte	10
Slag	5
Waste gases	up to 17
	<hr/> Sum total 100

53. Matte Smelting from Concentrates

Copper concentrates mainly consist of particles measuring 0.05 to 0.1 mm in diameter. If charged into a blast furnace directly the fine material would form a dense bed nearly impermeable to air, and it would be impossible to eliminate as much sulphur during smelting as would be necessary. The actual practice is therefore to roast copper concentrates prior to smelting.

On the other hand, roasting may well be dispensed with where the sulphur content of a concentrate is low or where sulphide concentrates may be smelted in a mixture with oxidised or mixed ores. In both cases, however, the heat given up by the chemical reactions is not sufficient for smelting, which fact necessitates the addition of fuel in concentrate smelting.

The Roasting of Copper Concentrates. The purpose of roasting is to oxidise the sulphide content of the concentrate, thereby reducing the proportion of sulphur in the charge to a point where a sufficiently rich matte may be obtained. Heated to kindling point, the sulphides burn spontaneously and liberate heat in accordance with reactions which, in a general case, may be presented for a bivalent metal as follows:



The oxidation of the sulphide by atmospheric oxygen produces a more or less dense film on the surface of sulphide grains (Fig. 76).

For the oxidation to go on, a continuous exchange is essential between the solid and gaseous phases, i.e., free access for oxygen to the sulphide, and withdrawal of sulphur dioxide. This is accomplished by the diffusion of the gases through pores and discontinuities in the oxide envelope over the sulphide grain.

As roasting progresses, the oxide film grows in thickness, and the gases find it increasingly more difficult to penetrate it; the combustion of the sulphide slows down or stops altogether. Of course the latter alternative is less likely to occur with finer than with larger particles which may have a thicker oxide film. Therefore,

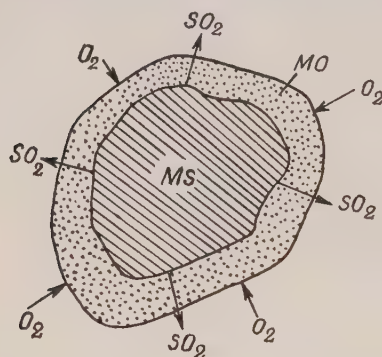


Fig. 76. Diagram showing oxidation of a grain of a sulphide mineral

roasting may be speeded up by grinding, as this increases the ratio of surface area to unit weight of the sulphide.

The rate of gas diffusion through pores and discontinuities in the oxide film rises with temperature; its rise, however, is usually kept within some limit to avoid fusion of the particles.

The rate of diffusion is furthermore dependent on the difference in the partial pressures of the oxygen and sulphur dioxide at the interface of the oxide film (Fig. 76), rising with decreasing SO_2 and with increasing O_2 in the gases surrounding sulphide particles; the rate of roasting is affected in a similar way. Therefore, the particles falling down or floating in the gas are roasted quicker than those lying in the bed. The roasting of the latter may be accelerated by stirring.

The heat given up by sulphide combustion goes to raise the temperature of the burning grains, although the bulk of heat is given up to the surroundings. At high rates of roasting, which is true of falling or floating particles, the rate of heat input per unit time appreciably rises, while the rate of heat exchange with the surroundings remains nearly unchanged. Therefore, heat is accumulated in the grains, raising their temperature and that of roasting.

Sulphide minerals widely differ in ignition temperature (Table 15) which is also affected by grain size, being higher for bigger than for smaller particles.

Table 15
**Ignition Point of Sulphides for 0.06 mm
Fineness**
(Courtesy the Urals Polytechnic)

Mineral	Chemical formula	Ignition point, °C
Pyrite	FeS ₂	360
Chalcosite	Cu ₂ S	435
Galenite	PbS	755
Sphalerite	ZnS	645
Molybdenite	MoS ₂	490

The average grain size of flotation copper concentrates is about 0.07 mm. The principal combustible constituent in them is pyrite which runs 40 to 50 per cent. In burning, 1 kg of pyrite generates 1607.0 kcal which is quite enough for the sustained combustion of the concentrate. No extraneous fuel is required, and roasting is a relatively cheap operation.

Copper concentrates are usually roasted in mechanically-rabbed multiple-hearth roasters.

A copper roaster is a vertical brick-lined steel-plate shell 9.6 m high and about 6.5 m in diameter, which supports several firebrick arches or hearths spaced 0.8 m apart. As a rule, 8, 10 or 12 hearths are provided, which are numbered from top to bottom (Fig. 77). The topmost open hearth is called the dry hearth and is not included in the total number of roasting hearths.

The central hollow shaft carries arms and rabbles which turn over and advance the concentrate across each hearth in succession. The lower end of the shaft is supported by a pivot. A short distance above the pivot, a toothed wheel is seated on the shaft, driven via a reducing gear at a speed of two or three revolutions per minute.

Usually two (or, which is seldom, four) rabble arms are mounted over each hearth. The rabbles are arranged at an angle to the axis of the arm. So, in rotating, the rabbles both turn over and move the material from centre to periphery on even hearths and from periphery to centre on odd hearths.

The concentrate is continuously fed by a mechanical feeder to the centre of the dry hearth and is gradually rabbled onto the first

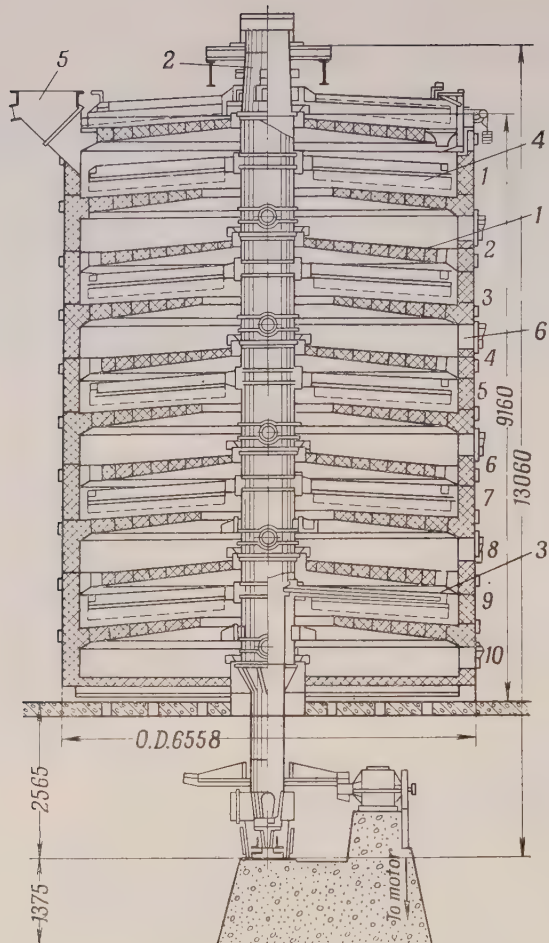


Fig. 77. Multiple-hearth roaster:

1—hearths; 2—central shaft; 3—rabble arm; 4—rabble; 5—gas off-take; 6—charging doors

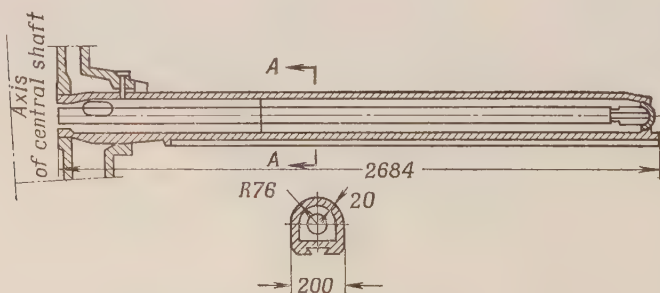


Fig. 78. Rabble arm

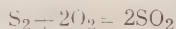
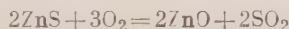
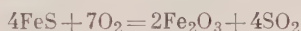
roasting hearth. On the first hearth the material is moved towards a circular hole through which it is dumped onto the second hearth, etc. Thus rabbled, the concentrate is caused to pass through all of the furnace to be discharged from it at the bottom. The air necessary to oxidise the sulphides is sucked in through openings. The exhaust gases rise against the flow of the concentrate retracing the same zig-zag path, and leave the roaster through the top hearth flues.

In starting up a roaster, the middle and bottom hearths are heated either by burners or temporary fireboxes which are put out as soon as the concentrate ignites. As an alternative, the cinder may be used for this purpose.

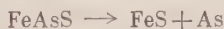
The maximum temperature of roasting (850°C) is attained on the middle hearths. A higher temperature is dangerous in that the concentrate may fuse together, causing damage to the rabble arms.

For longer service life, the rabble arms are cooled with air. The rabble arm, shown in Fig. 78, consists of two concentric pipes, the outer pipe being plugged and carrying the rabbles. Cooling air is admitted into the arm through the inner pipe and is discharged into the hollow central shaft or directly into the roaster. Both the arms and rabbles are of heat-resistant cast iron.

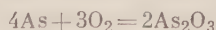
As it moves down the roaster, the concentrate is gradually heated to the temperature at which the sulphides are ignited or the higher sulphides are decomposed to simple sulphides and sulphur:



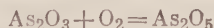
Like higher sulphides, arsenopyrite is decomposed as follows:



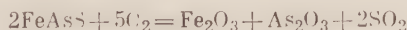
Arsenic is volatile; it vaporises to be oxidised to As_2O_3 :



With a considerable excess of air, it is further oxidised:



Direct oxidation of arsenopyrite is also possible, but the final result is the same:



The pressure of As_2O_3 fumes reaches 1 atm at 460°C , and it is easily carried off with the flue gases. On the other hand, the pressure of As_2O_5 fumes is relatively low; furthermore, this oxide reacts

with basic oxides, such as FeO or CaO, to produce arsenites of the type $xMO \cdot yAs_2O_5$. The greater the excess of air during roasting, the greater the proportion of arsenic oxidised to arsenites and left in the cinder.

The sulphur dioxide is partly oxidised by the excess oxygen to sulphur trioxide. The latter may react with some metal oxides to produce sulphates stable at elevated temperatures, such as lead and calcium sulphates.

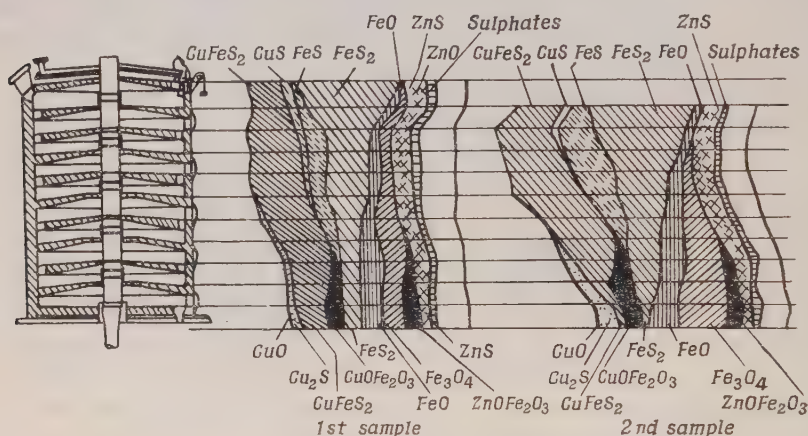
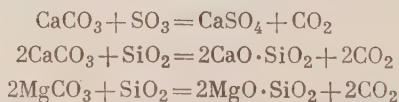


Fig. 79. Progress of copper-concentrate roasting (after Smirnov)

The solid constituents of the roasted concentrate react with one another. The acid oxides SiO_2 , Fe_2O_3 and SO_3 react with the basic oxides FeO, MgO, CaO, Cu_2O , etc., to produce ferrites $xMO \cdot Fe_2O_3$, silicates $yMO \cdot SiO_2$, etc.

The presence of SO_3 and SiO_2 promotes the decomposition of the carbonates:



As often as not, the reactions between the solids fail to reach completion due to lost contact, and roasted concentrates frequently contain a considerable quantity of original materials and the final products. Fig. 79 illustrates changes in the phase composition of the concentrate during roasting (after Smirnov).

The temperature in roasting furnaces depends on the sulphur content of the concentrate, the quantity of concentrate charged per unit time, and the volume of air fed into the furnace. In turn, it governs the daily output of a furnace which increases with increas-

ing temperature. It should be remembered, however, that copper concentrates may be sintered due to the formation of $\text{Cu}_2\text{S-FeS}$ alloys which melt at 960 to 1000°C. To avoid this possibility, account should be taken of the low-melting constituents of the concentrate.

Another limitation is that at some places within the roaster, especially near a moving rabble, the temperature may rise to well above the average for the concentrate body. For this reason, it is customary to limit the roasting temperature to 850°C.

The fusion of the concentrate may be prevented by mixing it prior to roasting with fluxes suitable for subsequent smelting and containing mainly quartz, limestone and flue dust.

The quantity of air admitted into the roaster should be such that the waste gases will contain not less than 4 per cent SO_2 , or else they will not be suitable for sulphuric acid production. Furthermore, too much air increases dust formation. Normally, the waste gases carry off with them 5 to 15 per cent of the material being roasted. The dust is caught by cyclones and electric precipitation filters, and so the final loss to dust does not exceed 0.5 per cent.

The current trend in roasting copper concentrates is away from multiple-hearth mechanically-rabbed furnaces towards fluidised-bed reactors. Against the 150 to 170 kg of sulphur eliminated per cubic metre per 24 hours in the former, the latter eliminate up to about 750 kg of sulphur. The SO_2 content of the waste gases, too, is 12-14 per cent in the latter as compared with not over 7 per cent in the former.

The net result of roasting is that the sulphide content is materially decreased and that of Fe_2O_3 and Fe_3O_4 increased. The temperature of the hot calcine is anywhere from 600 to 700°C. For a more streamlined operation, roasters are often located directly above reverberatory furnaces.

Concentrate Smelting in Reverberatory Furnaces. The reverberatory furnace for smelting copper concentrates shown in Fig. 80 is 35 to 40 m long, 7 to 10 m wide and 3.5 to 4.5 m high. The materials that go to build a reverberatory furnace may be either acid or basic, depending on which oxides—acid or basic—are predominant in the charge. The walls and roof are of silica or magnesite brick. The compatibility of the charge and refractory materials is essential as it extends the service life of the lining. Silica roofs are made of the arched type and magnesite roofs of the suspended type (Figs. 81 and 82). Suspended roofs are more advantageous than arched roofs. They are built of separate blocks (Fig. 82) suspended over the hearth, which fact simplifies furnace repair and maintenance as defective blocks may be easily replaced. The magnesite and heat-

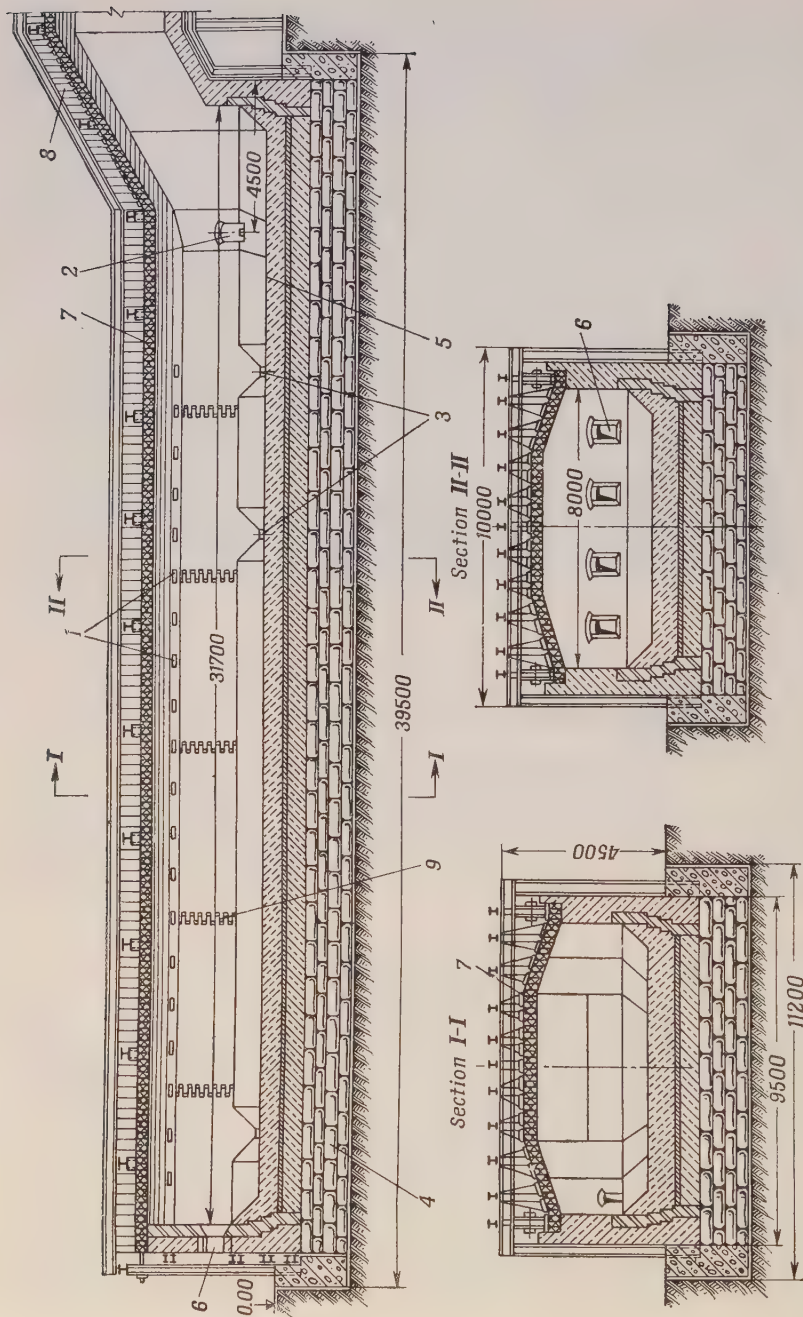


Fig. 80. Modern reverberatory furnace with a suspended roof for matte smelting:

1—charging doors; 2—slag spout; 3—tap holes; 4—foundation; 5—hearth; 6—burner ports; 7—suspended roof; 8—flue; 9—expansion joints

resistant chrome-magnesite brick used for suspended roofs is more refractory than silica brick. Unfortunately, it is more expensive.

For greater durability, the hearth is of quartz sand. The sand is given a preliminary heating to 1500-1600 C, when quartz (sp. gr. 2.65) transforms to tridymite (sp. gr. 2.24)*, and is then levelled and sintered into place producing a dense mass.

The furnace walls are ironed and stayed by I-beams placed in pairs along the walls or riveted steel columns spaced on 0.9-1.2-m

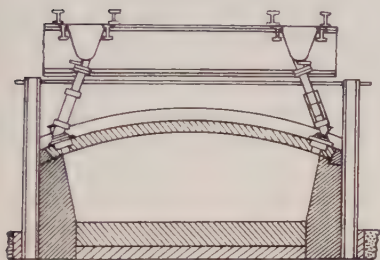


Fig. 81. Arched roof of a reverberatory furnace

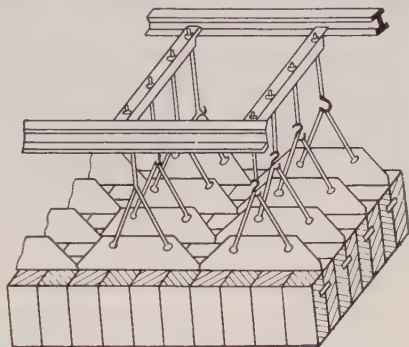


Fig. 82. Suspended-roof block of a reverberatory furnace

centres. The opposing pairs of beams are held together by tie rods placed above the roof. As the furnace rises in temperature, the nuts of the tie rods are backed off.

The brickwork has expansion joints to compensate for thermal expansion and contraction (see Fig. 80).

Reverberatory furnaces may be fired with fuel oil, pulverised coal or natural gas.

Pulverised coal or fuel oil is fed into a furnace by burners through openings in the front end wall. As a rule, the burners (of which there usually are 4 to 10) are arranged in a single row. The "primary" air, which goes to feed and disperse the pulverised coal or liquid fuel, is blown by an airblower under a pressure of 200-250 mm w.g. The "secondary" air is blown through the annular space of each burner and is sucked in through holes nearby.

The calorific value of pulverised coal is lower than that of residual oil. In addition to it, it produces much ash. The ash settles onto the surface of the molten bath and may affect the chemical analysis of the product or, if the ash is refractory, heat transfer from the gases to the molten bath may be impaired. Yet, being

* Tridymite is one of the three most important polymorphic crystalline modifications of silica, the other two being quartz and cristobalite.

much cheaper than residual oil, coal is used by the majority of copper-smelting mills. To reduce the effect of ash, it is important to burn a grade of coal with a calorific value of not less than 6000 kcal/kg, having not more than 15 per cent ash and over 25 per cent volatile matter.

The gases in a reverberatory furnace are hottest within about 3 to 10 metres of the front wall, reaching 1500 to 1550°C. Half the way down the furnace, the temperature falls to 1400-1350°C, and to 1250-1300°C at the rear wall.

As little as 30 per cent of the heat is recovered from the waste gases inside the reverberatory furnace. For a further recovery they are often passed through waste-heat boilers in which case heat recovery rises to 55-60 per cent. Sometimes the waste gases go to preheat the secondary air.

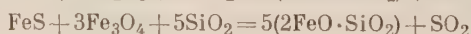
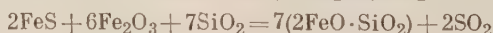
The charge is introduced into the reverberatory furnace through charge holes in the roof, usually located along the side walls for about half the length of the furnace. The object of charging along the side walls is to keep them covered with the charge and thus protect them from the action of the hot gases. The materials to be charged come from hoppers located above the charge holes, and to the hoppers they are delivered by cars or conveyers.

Molten converter slag is introduced down a runner the end of which is let into an opening in the fore part of a side or a front wall.

The molten products—the matte and the slag—are tapped at regular intervals. The slag is withdrawn through a slag spout in the rear portion (a side or the end wall) of the furnace, about 1 metre above the bottom. The requisite level of slag is maintained by a fireclay breast. The matte is usually tapped from two holes located at bottom level in one of the side walls (or, which is more seldom, in the front end wall). The tap holes are cast-iron or copper blocks with square openings into which cast-iron thimbles with an inside diameter of 45-50 mm are inserted.

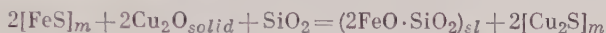
Modern reverberatory furnaces are usually operated by automatic control systems which maintain the desired fuel and secondary-air blows, temperature, and fuel oil pressure which are sampled at several points throughout the furnace. Automatic control reduces the consumption of fuel and fettling materials by 9 or 10 per cent and increases furnace output by 6 to 9 per cent.

Smelting of roasted concentrates. As the temperature of the charge rises, the following reactions begin in which the copper oxide and the higher iron oxides are reduced and slagged:



The silicates melt, flow down to melt the other oxides, and finally form slag.

The sulphides of copper and iron are melted together to produce the primary matte which flows down, loses some of its iron and picks up more copper:



Three or more ingredients usually take part in the above reactions of reverberatory smelting, which fact calls for the thorough mixing of the charge.

On smelting, the sulphur of the charge is usually oxidised by the oxygen of the higher oxides, its oxidation by the oxygen of the hot gases being very unlikely due to its scarcity in the products of fuel combustion. It is believed that the smelting of roasted concentrates eliminates 20 to 25 per cent of the sulphur that has been left by roasting.

The precious metals, such as gold and silver, are well soluble in the molten matte and nearly insoluble in the slag. For this reason, gold-bearing ores, their concentrates and other gold-bearing materials make good fluxes for reverberatory smelting. It should be noted that the fluxes should be added to the concentrate during the roast.

The reactions between the oxides and sulphide of iron are important for the reason that the Fe_3O_4 and the other ferrites should be reduced to the greatest possible extent, for they are almost insoluble in the slag (see above). If the ferrites fail to be reduced to completeness on the sides, the reaction will go on at the interface between the matte and the slag. The bubbles of the sulphur dioxide evolved in the process will carry matte particles into the slag. Therefore, there will be no clean separation between the matte and the slag, and more unsettled matte will be lost with the slag.

Smelting of green (unroasted) concentrates. This working is resorted to when a concentrate carries little sulphur, or when a high-grade concentrate is involved. It also applies to concentrates of oxide and mixed ores. The charge consisting of concentrates and small additions of fluxes is thoroughly mixed in mixers and introduced into the furnace. As the temperature of the charge rises, the higher sulphides give up their sulphur which is immediately burned and carried off by the gases as SO_2 . For this reason, desulphurisation reaches 45-50 per cent. Reactions between the sulphides and the oxides are possible, but they are not characteristic of green-concentrate smelting, because the charge contains small quantities of oxides. Green-concentrate smelting requires more fuel, for the charge is cold and often damp. The losses with dust are lower, but the output of the furnace is reduced. Much of the sulphur is lost poisoning the atmosphere around the works. The principal advan-

tage of green-concentrate smelting is a reduction in the loss of gold and copper. Some of the leading copper-smelting works in the Soviet Union, the United States, Chile and Africa use a dry (not roasted) charge.

The products and economics of reverberatory smelting. The slag is tapped intermittently through the slag spout by breaking the refractory breast. The slag is poured into a ladle and taken either to the dump or for granulation. If it does not carry any valuable constituents, the granulated slag is utilised in building or for the back-filling of mine workings. Sometimes, it is cast into blocks for use in road construction.

Twice to three times as much slag is produced in reverberatory smelting as matte by weight, the ratio by volume being 3 or 5 to 1. In assessing the copper losses with the slag it is important therefore to take into account both the copper content and the quantity of slag produced.

The reactions between the ferrites and iron sulphide fail to reach completeness prior to melting, and some of the ferrites enter the slag, especially the magnetites, and so the slag loses some of its fluidity when molten. Zinc sulphide acts on the slag in a similar manner. The solubility of Fe_3O_4 and ZnS in the slag depends on its composition and temperature.

The following is an approximate composition of the slag (in per cent) of reverberatory smelting:

Cu	SiO_2	FeO	CaO	Al_2O_3	MgO	S	ZnO
0.35	45.0	26.7	14.2	11.8	—	0.5	—
0.30	37.4	36.0	4.2	8.3	2	1.0	3.5
0.20	32.0	44.8	6.0	10.2	0.4	—	2.0

The matte is tapped as it accumulates. Between tappings, the holes are plugged by fireclay through which a bar is passed. The bar is pushed in as its end melts off. To tap the matte, the bar is knocked out or heated up with current and removed. The matte flows down a runner into a ladle which is then carried by an overhead crane to the converter bay.

Higher grades of matte are not attractive economically to produce by reverberatory smelting, because of increased copper losses in the slag. The usual practice is to produce mattes containing 20 to 40 per cent copper. Green-concentrate smelting produces lower grades of matte than do roasted concentrates.

The approximate composition of the matte produced in reverberatory furnaces (in per cent) will be as follows:

Cu	Fe	S	Zn	SiO_2	Al_2O_3	$\text{CaO} + \text{MgO}$	Au, g/ton	Ag, g/ton
15.6	49.9	28.3	2.9	1.2	0.4	2.0	—	—
30.0	38.0	23.9	2.6	1.5	1.8	0.6	8.7	230
35.0	30.9	25.5	2.1	1.6	2.7	2.5	7.8	168
59.1	14.5	22.9	—	0.4	2.1	1.2	3.8	600

Owing to the small amount of slag produced in reverberatory smelting, 95 to 98 per cent copper and precious metals is withdrawn from the charge into the matte.

The performance of reverberatory furnaces is assessed in terms of daily output and fuel consumption. The latter is usually expressed in equivalent fuel (an arbitrary fuel having a calorific value of 7000 kcal/kg) as the percentage (by weight) of the charge smelted. The daily output of modern reverberatory furnaces ranges from 2.0 to 9.0 tons of charge per square metre of hearth area. The highest daily output is attained with hot roasted iron-bearing concentrates, and the lowest with green high-silica concentrates. In addition, daily output is also affected by fuel quality, furnace design, and workmanship. Fuel consumption usually is 9 to 25 per cent of the charge (by weight).

Other Methods of Concentrate Smelting. Copper concentrates may also be smelted in suspension. An installation for this process will include an ordinary reverberatory furnace and a suspension roaster*. The main advantage of this process is the more complete utilisation of the heat generated by roasting, which fact makes it possible to reduce fuel consumption in actual smelting. Developed in the Soviet Union, this process is being used by some foreign smelters. At one of them roasting uses commercial oxygen, and no fuel is burned at all. The waste gases carry up to 75 per cent SO_2 which is collected, liquefied and sent for use at paper-making factories.

Another method for smelting copper concentrates is in electric furnaces. Although it offers a number of advantages, its use is limited because of the high cost of electricity. The higher temperatures attainable in electric furnaces considerably speed up the smelting, and produce high-silica slags of low specific gravity and high fluidity when molten. There are no waste gases, and the dust losses are considerably lower.

The consumption of electricity per ton of charge is 400 to 500 kWh. The daily output is about the same as of reverberatory furnaces.

The construction and operation of electric furnaces as used for the smelting of sulphide copper-nickel ores and concentrates are described in Chapter VII.

54. Converting

After the copper and other valuable constituents of the ore have been concentrated into the matte and the earthy material into the slag, the next step in copper manufacture is to remove the iron

* See the chapter, "The Metallurgy of Zinc".

and sulphur of the matte by oxidation. This is accomplished in a vessel known as a converter.

A modern copper *converter* is a horizontally placed cylindrical furnace measuring 4.3 to 10 m in length and 2.3 to 4 m in diameter. The air for the oxidation is introduced through the side of the converter by means of tuyeres. The shell of the converter (Fig. 83) is lined with magnesite brick and is carried by two plain rims and one toothed rim. The plain rims are supported each by two pairs of rolls mounted on swinging pedestals. The toothed rim engages a drive gear which is actuated by a motor. With this arrangement, the converter may be turned a complete revolution in either direction.

The matte is introduced, the slag and blister copper withdrawn, and the gases pass to the stack through a conical mouth provided in the middle of the vessel.

In the working position the mouth points upwards and is placed beneath an iron hood having a connection with the stack. The edges of the hood are cut to fit the outline of the converter. Fitting closely to the converter shell, the hood prevents the excessive dilution of the waste gases with atmospheric air. Sometimes, the hood may have a lifting front wall for better sealing.

Converters operate intermittently and produce up to 100 tons of copper per charge.

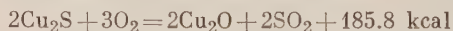
The *operation of converting* consists of two stages: first, the elimination of the iron, or blowing to white metal; and second, the elimination of the remaining sulphur, or blowing to blister.

To start a converting operation, the converter is turned so that the tuyeres are above the molten bath, the proper amount of matte introduced (at about 1200°C), the blast turned on, and the converter turned to place the mouth under the hood taking the gases to the stack.

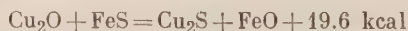
During the first stage, the air blast stirs the bath vigorously (Fig. 84), and the iron sulphide is oxidised on the surface of the bubbles to FeO:



The copper sulphide is oxidised according to the reaction:



The cuprous oxide is immediately resulphurised by reacting with the iron sulphide:



The FeO is slagged by the quartz which is added as soon as the blast is turned on:



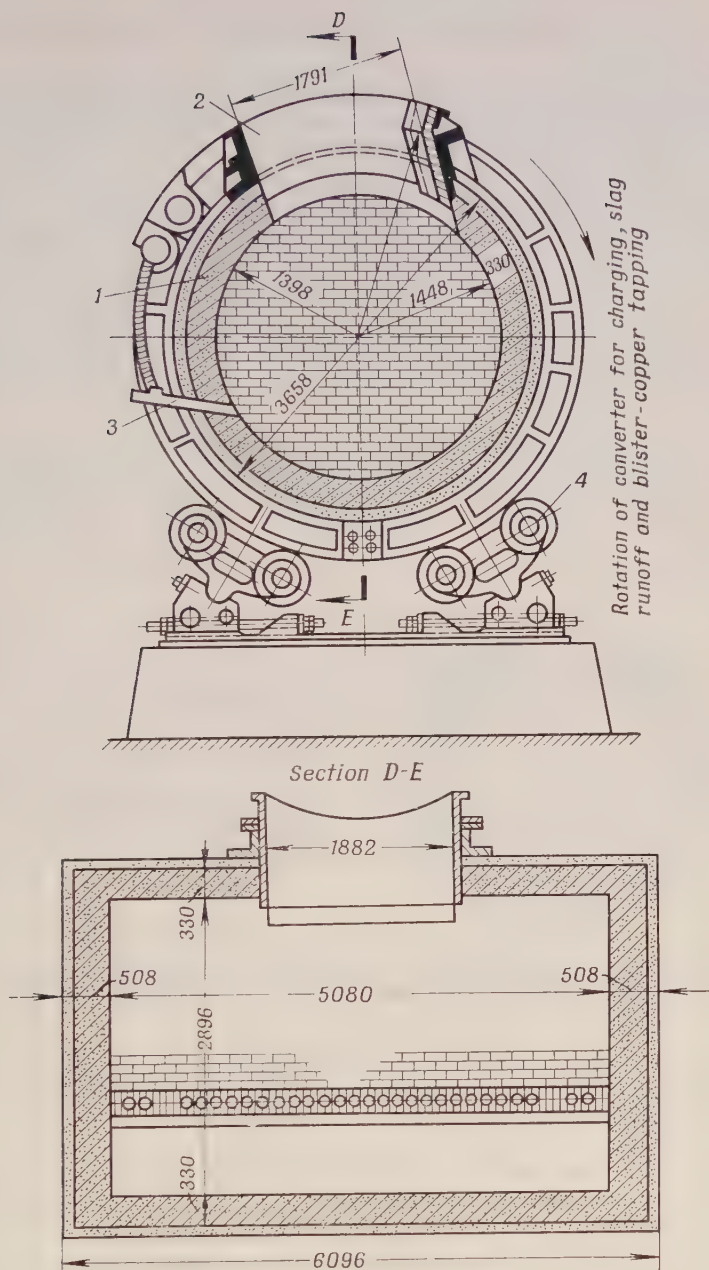
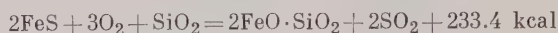
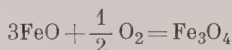


Fig. 83. Copper-matte converter:
 1—lining; 2—nose or mouth; 3—tuyere; 4—roller stand

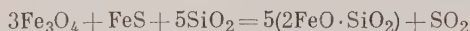
The oxidation of the iron sulphide in the matte in the presence of silica, which is the principal source of heat in the converter, may be described by a combined reaction:



If too little quartz is present, magnetite may be formed:



The ferrites, including magnetite, may be reduced by the iron sulphide of the matte in the presence of quartz according to the reaction:



For this to take place, finely divided quartz (6-12 mm across) should be spread uniformly over the matte and a sufficiently high

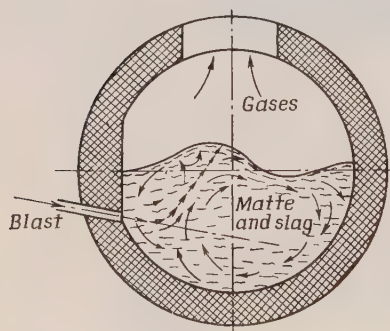


Fig. 84. Diagram of converting

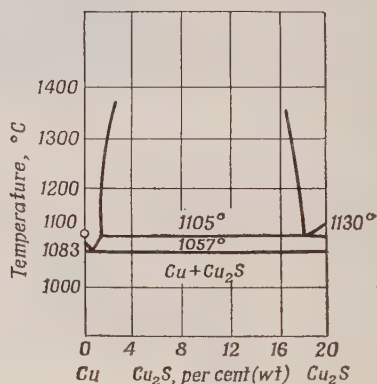


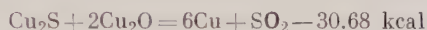
Fig. 85. Constitution diagram of the system Cu-Cu₂S

temperature maintained in the converter. Normally, the temperature during the blow to white metal should be 1250-1350°C. It should be neither higher, or the lining may be scoured, nor lower, or the slag will not be sufficiently fluid. It may be raised by adding fresh hot matte and reduced by adding a cold charge. If not reduced, the ferrites will pass into the slag as solid suspended particles, making it sticky and increasing the copper loss.

As the oxidation proceeds and the iron is slagged, the matte in the converter gradually approaches white metal (Cu₂S). When the iron has been slagged, the converter is turned down, the blast is turned off, and the slag is skimmed into a ladle.

To avoid sputter, the converter is usually filled one-third full. Therefore, after skimming the slag, a fresh charge of matte is introduced and the operation repeated (which is known as doubling). The procedure is repeated until the amount of remaining white metal is sufficient for blowing to blister, or the second stage. The first stage usually occupies from 6 to 24 hours.

During the second stage, the blast is again turned on, the sulphur in the white metal is oxidised, and the oxidised copper reacts with the remaining white metal to produce metallic copper and sulphur dioxide:



The small amount of iron left over from the first stage is oxidised at the beginning of the second stage, producing a small amount of slag high in copper. After the blister is tapped, this slag is left in the converter for the next operation. The blow to blister usually lasts for 2 or 3 hours.

Referring to the constitution diagram of the system Cu-Cu₂S (Fig. 85), at the converting temperature (1250°C) the copper formed initially dissolves in Cu₂S, and the molten metal in the converter remains single-phase. As the oxidation proceeds, the bath separates into a copper solution in Cu₂S and a Cu₂S solution in copper. When the amount of Cu₂S in the converter is reduced to its limit of solubility in copper, the bath again becomes a single-phase solution of Cu₂S in copper.

The equilibrium constant for the above reaction, disregarding the mutual solubility of the reactants, may be expressed through the equilibrium pressure of SO₂, or $K_{eq} = P_{\text{SO}_2}$:

Temperature,	deg. C	700	900	1100	1300
$K_{eq} = P_{\text{SO}_2}$,	atm	0.64	2.25	10.0	169.0

The reaction will proceed if the partial pressure of SO₂ in the gases above the molten bath is less than equilibrium pressure. Even if the oxygen of the blast were fully utilised, the partial pressure of SO₂ could not be higher than 0.21 atm (the air contains 21 per cent oxygen, and one molecule of O₂ can produce one molecule of sulphur dioxide). From the values of the equilibrium constants it follows that the reaction producing metallic copper may begin at as low as 700 C. At the temperature attainable in the converter (about 1250°C) it proceeds vigorously. Taking into account the activities of Cu₂S and Cu₂O in copper, the equilibrium constant for the molten white metal may be rewritten as follows:

$$K = \frac{a_{[\text{Cu}]}^6}{a_{[\text{Cu}_2\text{O}]}^2 a_{[\text{Cu}_2\text{S}]}} P_{\text{SO}_2}$$

Towards the end of the converting operation the activity of Cu_2O reaches a constant value, and that of copper may also be considered constant. Consequently, the pressure of SO_2 will be directly proportional to the remaining Cu_2S in the copper. The oxidation of Cu_2S stops when the equilibrium pressure of SO_2 has reached a value slightly above 1 atm. If the reaction is to proceed further, the bubbles of sulphur dioxide should overcome the atmospheric pressure and the hydrostatic pressure of the molten metal above. The total pressure is greater than 1 atm even on the surface of the molten bath, and some sulphur will therefore be always left in the resultant blister.

The slags of the converting process contain a total of 75 to 90 per cent iron oxide and silica. The remaining constituents come from the gold-bearing quartz sand used as flux. From the data for several copper smelters the following average composition of the converter slag may be derived (in per cent):

SiO_2	FeO	Al_2O_3	Cu
17-28	60-70	3	1.5-2.5

Relatively acid slags contain less magnetite, and copper losses are lower.

The converter slag is too rich in copper to be thrown away and is returned to the reverberatory furnace or to the blast-furnace settler for additional treatment. In some cases, the slag is poured on a floor, allowed to solidify, and crushed. The crushed slag is then added to the ore charge of the blast furnace.

The waste gases of the blow to white metal carry 12-15 per cent SO_2 and about 0.2 per cent excess oxygen. The SO_2 content of the gases given up during the blow to blister is 15-17 per cent. In both cases, the gases are good enough for the manufacture of sulphuric acid or sulphur, but they are used for this purpose very seldom. For one thing, converters operate intermittently, and for another, the gases are diluted due to leaks at the joint between the hood and the converter shell. Though developed, gas-tight hoods have not yet found any appreciable use.

The dust carried by the converter gases consists of solidified matte and copper drops, flux particles, and the volatile oxides of impurities. The proportion of copper and precious metals contained in the dust may be as high as 5 per cent of the respective amounts in the original charge. For the most part, the copper and precious metals are in the form of coarse particles and can be easily recovered in simple settling chambers; the dust thus recovered is returned to the converter or the reverberatory furnace. Fine dust may be recovered by electrostatic precipitators past settling chambers. The fine fraction mainly consists of oxides of lead, zinc and rare metals.

After the blow, the blister copper is tapped from the converter into a ladle which is then carried by an overhead crane to the casting area. Where small quantities of blister copper are produced, the casting may be done directly from the ladle into stationary rectangular steel moulds. Where much blister copper is produced, a conveyor-type casting machine has found use.

Blister copper may contain up to 98.5-99 per cent of the copper and precious metals present in the original matte, including the recovery from the slag, the percentage being higher for higher grades of matte.

Currently, work is well ahead on applying automatic control to converters. With automatic control, it will be possible to obtain waste gases very high in sulphur dioxide by suitably regulating blow pressure and the pressure in the hood. An automatic controller would be able to turn the converter in the case of a drop in blow pressure, thereby preventing the flooding of the tuyeres by matte. Experience has already shown that with automatic control the waste gases are well suited for the manufacture of sulphuric acid.

55. Scrap (Secondary) Copper

After sorting, copper scrap and wastes are resmelted in reverberatory or electric furnaces into a variety of copper-base alloys. If necessary, the molten metal is refined, deoxidised and alloyed with the deficient additions; the alloy is cast and shipped to the user.

Difficult-to-sort wastes (or wastes widely differing in analysis) are resmelted to copper while their valuable constituents are recovered as by-products. The resultant metal is called secondary copper.

Prior to resmelting, the wastes are classed according to size, and the fines are agglomerated on sintering machines. The pieces that go into the charge measure 100 to 400 mm across.

Scrap copper is resmelted in small blast furnaces with coke as fuel and quartz and limestone as flux. The coke accounts for 12 to 17 per cent of the charge by weight.

Copper oxides are easy to reduce, and so a slightly reducing atmosphere is only necessary for resmelting. The zinc oxides are reduced in the lower levels of the charge. Some of the zinc and lead vaporises and passes off in the waste gases. The bigger proportion of zinc and lead, however, goes to the slag and the matte. The dust loss amounts to 3 or 4 per cent of the charge by weight.

Most of the impurities present in the secondary copper are eliminated by blowing it in a converter. The heat necessary for converting is supplied by the oxidation of the impurities and the combustion of the coke added to the charge. The coke consumption usually is about 5 kg per ton of copper treated.

The zinc, lead and tin oxidised by the converting operation are withdrawn into the slag and dust. The amount of dust produced is 6 to 7 per cent of the copper smelted (by weight). The dust is treated separately.

The slag from the converting process is cooled, broken up to pieces and used in copper-blast furnaces. The zinc content of the converter slag reaches 18-20 per cent.

56. The Refining of Blister Copper

The blister copper produced in the smelting process contains so much impurities iron, sulphur, oxygen, zinc, nickel, arsenic, antimony, etc., that it has to be refined before it is suitable for commercial use. The following table shows the average composition of blister copper smelted from primary and secondary raw materials (in per cent):

	Primary copper	Secondary copper
Cu	98.6-99.3	97.5-98.2
Fe	0.01-0.04	up to 0.05
Ni	0.005-0.6	0.3-1.0
S	0.05-0.1	—
Zn	0.01-0.05	up to 0.5
As	0.01-0.1	—
Sb	0.01-0.1	up to 0.3

Blister copper also contains lead, selenium, tellurium, gold, silver and dissolved gases which even in small amounts adversely affect the mechanical properties of copper, especially ductility. All impurities (except for precious metals) reduce the electrical conductivity of copper.

The content of gold and silver in blister copper is often as high as 100 and 2000 grams per ton, respectively. Their recovery is attractive economically and is done during the refining operation.

Commercial copper in the Soviet Union is available in five grades (Table 16).

Crude blister copper may be refined by (a) the fire process and (b) the electrolytic process.

Fire refining produces Grades M3 and M4 and is unable to recover bismuth and precious metals. Electrolytic refining, on the other hand, removes any gold and silver contained in the blister copper and produces refined copper of highest purity. The greater capital outlays involved in electrolytic refining are fully compensated for by the gold and silver recovered.

On account of its purity, by far the larger proportion of copper is refined electrolytically. In order to further raise the purity of

Table 16

Chemical Analyses of Commercial Copper Grades
(per cent)

Copper grade	Min. copper content	Max. impurities										
		Bi	Sb	As	Fe	Ni	Pb	Sn	S	O	Zn	total
M0	99.95	.002	.002	.002	.005	.002	.005	.002	.005	.02	.005	.05
M1	99.90	.002	.002	.002	.005	.002	.005	.002	.005	.08	.005	.1
M2	99.70	.002	.005	.01	.05	.2	.01	.05	.01	.1	*	.3
M3	99.50	.003	.05	.05	.05	.2	.05	.05	.01	.1	*	.5
M4	99.0	.005	.2	.2	.1	*	.3	*	.02	.15	*	1.0

Note: In the cases marked with an asterisk (*), the content of a given impurity may be as high as the difference between the total impurities and the sum of the remaining impurities.

refined copper and to reduce refining costs, crude blister copper is customarily fire-refined preparatory to electrolytic treatment.

Crude blister copper cast into slabs is taken to copper refineries, or it may be fire-refined where it is smelted, after which it is cast into anodes and shipped to electrolytic refineries. The latter arrangement is more advantageous in that the wastes of fire refining, high in copper, may be re-treated with matte in converters.

Fire Refining. The reverberatory furnaces in which the refining is conducted (Fig. 86) are similar in design to the reverberatory furnaces for the smelting of ore. They are built in capacities up to 400 tons of copper and measure 12 to 15 m in length, 5 m in width and about one metre in depth. The temperature required for fire refining is 1130-1170°C.

The hearth is constructed of silica or magnesite brick, encased in cast-iron plates, and set up on pillars. By this arrangement, molten copper is prevented from leaking through cracks and joints in the brickwork. The hearth bottom in acid furnaces is fritted with a mixture of finely divided quartz and copper mill-scale. In basic furnaces the materials used for the purpose are magnesite, limestone, quartz and iron mill-scale.

The walls of magnesite or high-alumina firebrick are faced with cast-iron plates on the outside, and ironed with I-beams. The rectangular charging holes are fitted with lifting doors.

The roof (which usually is of the arch type) is made of silica brick.

The fuel used may be fuel oil, natural gas or pulverised coal. The principal requirement for fuel is little, if any, sulphur present, for the sulphur dioxide in the flue gases may contaminate the refined copper. Large refining reverberatories are fired automatically, with both the fuel and air being fed in a preset ratio, depending on the required temperature in the furnace. Fuel consumption is 10-11 per cent of the charge by weight.

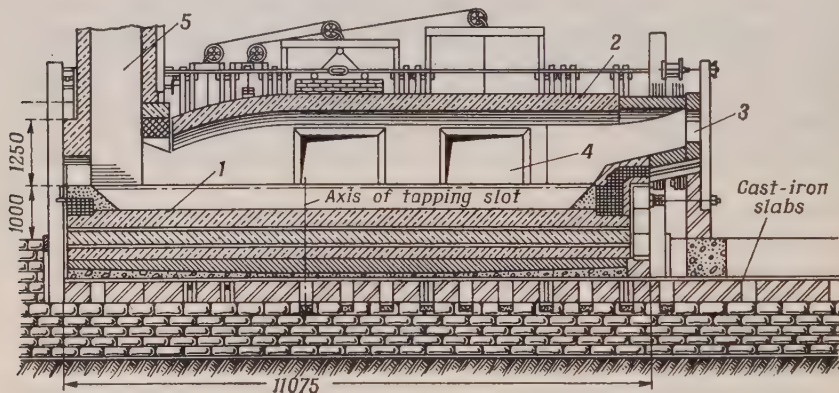


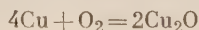
Fig. 86. Copper refining furnace:

1—hearth bottom; 2—roof; 3—burner ports; 4—charging doors; 5—flue

If copper is refined at a place other than where it is smelted, it takes 12 to 16 hours to refine a charge of blister copper. The various operations of the furnace may be classified as charging, melting, oxidising, poling and casting, and will be taken in that order.

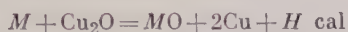
Slabs of copper are charged into the furnace by means of a paddle mounted on the cab of an overhead crane (Fig. 87). The paddle can take as much as 3.5 tons of copper slabs at a time. Molten copper is charged by means of a crane-handled ladle or a mixer truck holding up to 70 tons of copper.

After charging, the fire is raised to the utmost extent. Being an excellent conductor of heat, the copper rapidly melts. The impurities are oxidised by the air which is blown through lined iron pipes 20 to 40 mm in diameter inserted in the molten copper. The oxidation takes place on the surface of the air bubbles rising to the surface of the bath. The rate of oxidation depends on the concentration of a given metal, for which reason the copper is oxidised most of all:



The cuprous oxide quickly spreads throughout the volume of molten metal.

The oxidation of the impurities may be described by a generalised equation:



The oxides of the impurities float to the surface, forming a blanket of slag. The skimming of the slag withdraws much of the

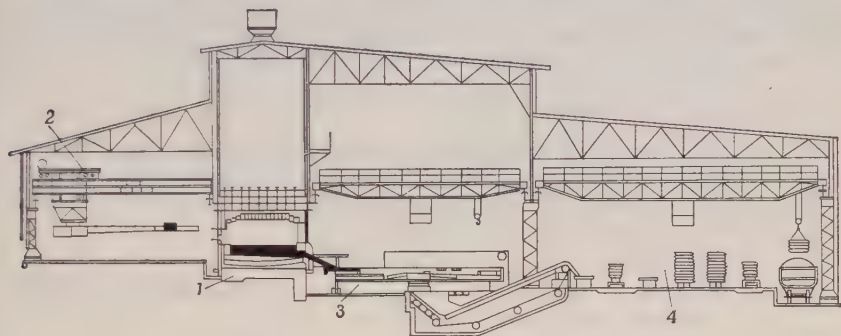


Fig. 87. Layout of fire copper refining plant:

1—copper refining furnace; 2—copper charging crane; 3—casting machine; 4—anode storage

remaining impurities, thereby facilitating the refining. The equilibrium in the oxidation of the impurities is attained when the dissociation pressures of cuprous oxide and of the oxides of the impurities are equal, i.e.:

$$P_{\text{O}_2}[\text{Cu}_2\text{O}] = P_{\text{O}_2}[\text{MO}]$$

At constant temperature the dissociation pressure of Cu_2O depends on its concentration in the molten bath. In fire refining, the dissociation pressure of Cu_2O is a constant value almost proportional to the concentration of a saturated solution and, consequently, to the dissociation pressure of solid Cu_2O . At 1084°C , the dissociation pressure of Cu_2O is of the order of 10^{-6} atm and 10^{-4} atm at 1200°C .

The dissociation pressure of the oxides of the impurities increases with decreasing concentration of the impurities in the copper and with increasing concentration of their oxides in the slag:

$$P_{\text{O}_2}(\text{MO}) = K \frac{a_{(\text{MO})}^2}{a_{[\text{M}]}}$$

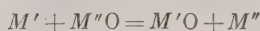
If $P_{\text{O}_2}(\text{MO}) = P_{\text{O}_2}(\text{Cu}_2\text{O})$, the equilibrium condition governing the remaining concentrations of the impurities in the copper may be expressed as follows:

$$[\text{M}] = \sqrt{\frac{K}{P_{\text{O}_2}(\text{Cu}_2\text{O})}} \cdot a_{(\text{MO})} = K_1 a_{(\text{MO})}$$

In this equation, the coefficient K gives a measure of the affinity of a given impurity for oxygen.

The oxidation is promoted by skimming the slag or by decreasing the concentration of free oxides in the slag by combining them into poorly dissociating compounds. This is the reason why better refining is obtained in acid furnaces, as the silica of the lining reacts with the oxides to form silicates.

The sequence in which the various impurities are oxidised depends on the fact that they may be oxidised not only by the cuprous oxide but also by the other oxides present in the molten bath:

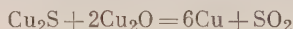


In this case, M' has a greater affinity for oxygen than M'' . In rough approximation, oxidability varies with decreasing affinity for oxygen, and metals will oxidise in the order given: Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb, Bi.

In reality, however, all impurities are burned out simultaneously though at different rates which depend not only on normal affinity for oxygen but also on concentration ratios, slagging ability, volatility, rate of oxidation, and some other factors.

Fire refining fails to remove the precious metals, because they have very weak affinity for oxygen. Bismuth is removed but to a negligible degree.

The sulphur in the copper is present as dissolved Cu_2S and is oxidised as follows:



Selenium and tellurium have a weaker affinity for oxygen than has sulphur. Therefore, furnace refining cannot eliminate them, and they persist in the copper as Cu_2Se , Cu_2Te , etc.

When the metal in the bath has been skimmed clean, a green pole is inserted in the bath to agitate the metal and drive out the sulphur held in solution by the copper as well as the dissolved sulphur dioxide and other gases. This operation is called poling down. It usually leaves up to 12 per cent Cu_2O , and the metal requires another operation of poling so as to improve its plasticity. The material used for the purpose is coke or charcoal spread on the surface of the bath. A pole is then inserted in the bath in order to reduce the cuprous oxide to metallic copper:



Gas bubbles rise to the surface of the bath, and the cuprous oxide is reduced to a trace content of 0.3-0.5 per cent without difficulty.

The poling of copper may be assisted by blowing producer gas into the molten metal.

It is important to skim off the slag prior to poling, or else the impurities stored up in the slag may be reduced from the oxides and pass into the copper as the amount of cuprous oxide in the bath is decreased:



When the poling is finished, the copper is now said to be "tough pitch" and is ready for casting. The duration of the refining depends on the scope of production and mechanisation. When the refining reverberatory is charged with molten blister copper fully or even

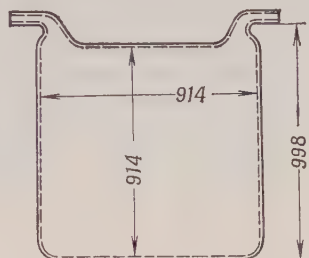


Fig. 88. Copper anode

partially, the refining time is appreciably reduced, since the melting accounts for about 30 per cent of the total time. In addition, less fuel is burned.

The metal is drawn off from the side or end of the furnace through a tapping slot. During the working of the furnace the slot is closed by a plug of fireclay. At the time of casting, the plug is cut away from the top sufficiently for the copper to flow over the edge into a launder and into a ladle. The metal from fire refining is cast into anodes for the electrolytic process (Fig. 88). This purpose is served by several types of casting machines. One of them is the Walker wheel. The moulds, which can be of cast iron or copper, are located on the circumference of a wheel turned by a motor, and the moulds are brought under the furnace ladle where they are stopped automatically while the mould is being filled. The wheel is then rotated to place another mould under the ladle. As the newly cast anode travels round the circle, it is sprayed with water to cool the metal and the mould. The ready anodes are placed in a bosh filled with running water in order to cool them to room temperature. After cooling, the anodes are taken to a storage room.

Average blister copper produces about 2 to 3 per cent of its weight of slag. The slag from refining in an acid furnace contains 15-40 per cent SiO_2 , 5-10 per cent Fe as silicates and ferrites, and oxides of zinc, nickel and other metals. The copper content of such a slag is 35 to 45 per cent. Four-fifths of this amount is present as cuprous oxide, and the remainder as metal drops which have failed to settle.

The slag from refining in a basic furnace contains 50 to 75 per cent copper and usually not over 5-10 per cent SiO_2 .

Refinery slag is reduced in small blast furnaces for matte and waste slag and in converters together with matte.

Electrolytic Refining. Copper anodes are placed in a tank filled with a solution of copper sulphate to which is added some sulphuric acid (the electrolyte). The cathodes are pure copper starting sheets suspended between the anodes. The anodes are connected to the positive and the cathodes to the negative terminal of a source of direct current. As current is passed through the electrolyte, the anodes are dissolved, the anode copper passes into solution, and the copper ions discharge at the cathodes to form a deposit of pure metal.

The anodes are usually made 40-50 mm thick and 250-320 kg in weight. The starting sheets are made by depositing copper on rolled and stretched copper blanks in an electrolytic bath. Sometimes, stainless steel blanks are used for the purpose. After thorough cleaning and prior to depositing, the blanks are coated with a mixture of graphite and oil. This coating is for the purpose of allowing the sheets of copper deposit to be readily stripped from the blanks. The blanks are usually held in the electrolytic bath for 24 hours. The blanks are then withdrawn, and one sheet from each side is removed, 0.2 or 0.3 mm thick.

The starting sheets are 30-50 mm wider and longer than the anodes. At the top edge, both the cathodes and anodes have riveted or welded lugs through which a copper bar is passed for hanging the plates and for supplying current to them.

The tanks used for electrolytic refining vary in size depending on the size and number of plates placed in them. Usually, there will be 45 starting sheets and 44 anodes. A typical tank measures 3 to 5 m in length, 1 to 1.1 m in width (12 to 13 cm wider than the starting sheets), and 1 to 1.3 m deep.

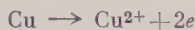
Electrolytic tanks are made of wood or concrete and are set up on reinforced-concrete piers high enough (up to 6 m) to permit proper inspection of the bottom for leaks and repair. The tank and the piers are separated by glass or porcelain insulators varying in shape to prevent current leakage.

Electrolytic tanks are now often assembled of prefabricated reinforced-concrete elements bolted together, while the bottoms are built up of wooden boards.

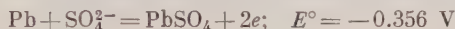
The walls of the tank are lagged by either PVC sheets welded at the joints by hot air or by lead sheets as a protection against the scouring action of the acid electrolyte. Sometimes, the tanks are ganged into cascades of 40 to 50 or even more, thereby effecting an economy of floor space and labour requirements.

The electrodes of two adjacent tanks are connected in series by means of a light bar on which the cathodes of the preceding tank and the anodes of the succeeding tank rest. For better contact, the bars sometimes have recesses. A diagram of the electric circuit in electrolytic refining is shown in Fig. 89, while Fig. 90 gives a sectional view of a tank and a part of a cascade.

When the current is turned on, the copper of the anode passes into solution:



As a result, the potential at the anode rises to $+0.34$ V, making possible the following electrochemical reactions:



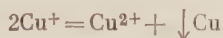
As current density, i.e., current per unit area, at the anode increases, the potential of the latter rises due to polarisation owing to the fact that copper ions are produced at the anode at a higher rate than they are released into solution by relatively slow diffusion. The concentration of copper in a thin layer near the anode increases, and the potential of the anode rises according to Nernst's equation:

$$E_{\text{Cu}} = E^\circ + \frac{RT}{nF} \ln a_{\text{Cu}^{2+}}$$

An increase in current density at the anode or at some places (when the anode dissolves non-uniformly) may promote some other reactions:



Experience has shown that a negligible quantity of single-charge copper ions is formed and little silver is dissolved. Besides, single-charge copper ions in the electrolyte behave as follows:



Silver dissolution is prevented by adding some sodium chloride to the electrolyte, and the silver is precipitated as AgCl . Gold will

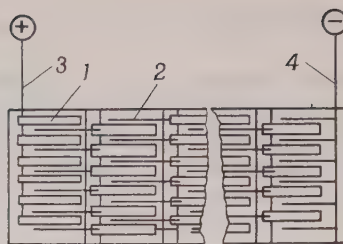


Fig. 89. Electric circuit of an electrolytic cell:
1—anodes; 2—cathodes; 3—anode bus; 4—cathode bus

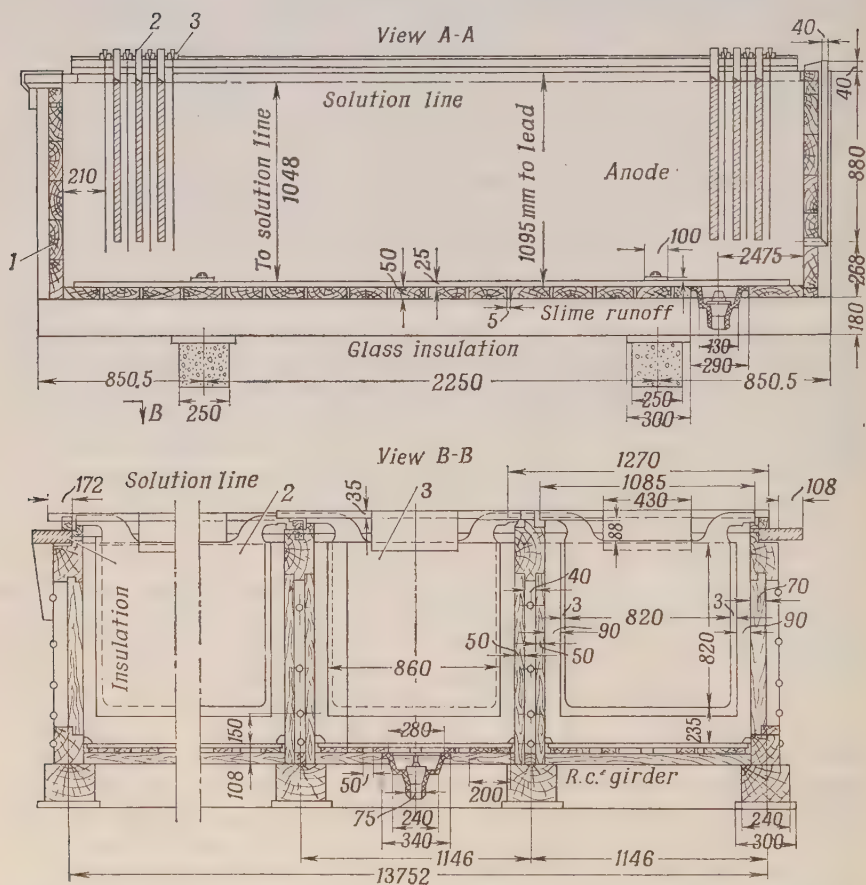


Fig. 90. Section through an electrolytic cell and part of a cell cascade:
1—cell; 2—anodes; 3—cathodes

not dissolve at the anode, for:



The impurities of sulphur, selenium and tellurium present in the copper as compounds of the type Cu_2R , where $R = \text{S, Se or Te}$, pass into the slime.

The principal reaction at the cathode is the reduction of double-charge copper ions:



The neutral atoms of copper thus produced form copper crystals which are deposited at the cathode to make a firm union with the copper of the starting sheet.

The impurities associated with the copper in the anode do not deposit at the cathode, for their discharge potentials are lower than that of copper. Therefore, the zinc, iron, bismuth, arsenic, nickel, tin and antimony of the anode copper are dissolved to remain in solution. Some metals, notably antimony and arsenic, are oxidised by atmospheric oxygen to form nearly insoluble compounds which either are deposited as a sludge or remain in solution as a suspension.

The copper deposit at the cathode may be contaminated by impurities through the entrapment of some electrolyte and suspended slime. To prevent slime accumulation in the electrolyte, it is withdrawn at regular intervals, purified and returned to the tank. Sometimes, the withdrawn electrolyte is purified at some other place, and the electrolyte in the tank is replenished with fresh diluted sulphuric acid.

The equilibrium potentials of the anode and cathode in electrolysis are practically the same as both are of copper and are placed in one and the same solution:

$$E_a - E_c \approx 0$$

The voltage necessary for the operation of the tank is the sum of the voltage required to cause ions to move from the anode to the cathode and the voltage which goes to overcome the e.m.f. of polarisation (counter e.m.f.). The former is expressed as IR , where I is the current in amperes and R is the resistance of the tank circuit in ohms, including the resistance of the electrolyte between electrodes, the resistance of the electrodes themselves, and the contact resistance where they are connected to the external circuit.

The resistivity of the electrolyte increases with increasing concentration of CuSO_4 , but sharply decreases as more sulphuric acid is added and the temperature raised.

This relationship suggests a practical method for reducing the required voltage. Electrolytic refining is conducted with an acid electrolyte heated to 50-55°C. Usually, the electrolyte contains 30-40 grams of Cu per litre and about 200 grams of H_2SO_4 per litre.

Counter e.m.f. is due to the fact that the concentration of copper ions at the cathode is lower, and at the anode higher, than in the electrolyte as a whole. Counter e.m.f. rises with increasing current density. One method for reducing counter e.m.f. is to increase the rate of circulation of the electrolyte.

The total voltage and the various voltages required for the operation of a copper-refining electrolytic tank are given in Table 17.

Table 17
Approximate Requirements in Voltage for
Electrolytic Copper Refining
(After Gayev and Yesin)

Resistances	Voltage drop	
	V	per cent
Electrolyte	0.23850	80.5
Counter e.m.f.	0.01597	5.3
Anode slime	0.02025	6.7
Cathodes and anodes	0.00337	1.1
Contacts	0.01829	6.4
Total	0.29638	100.0

Energy consumption is a major item in the cost of electrolytic copper. It is usually expressed in kilowatt-hours per ton of cathode copper, and is calculated on the basis of current efficiency.

Current efficiency is the ratio of the amount of product actually obtained to that theoretically obtainable in accordance with Faraday's law. Deposition of one gram-equivalent of copper ($\frac{63.57}{2} = 31.78$ grams) requires 26.8 A-h of current; one ton will take:

$$(It)_{theor} = \frac{1 \times 10^6 \times 26.8}{31.78} = 0.843 \times 10^6 \text{ A-h}$$

where I is the current, t is the time in hours, and $(It)_{theor}$ is the current required theoretically.

Current efficiency is always less than unity on account of various factors, such as short circuits in the tank, current leakage, and the deposition of impurities at the cathode, or:

$$K_c = \frac{(It)_{theor}}{(It)_{actual}}$$

The actual current requirements per ton of cathode copper will be

$$(It)_{actual} = \frac{0.843 \times 10^6}{K_c} \text{ A-h}$$

Then energy consumption will be the actual current consumption times the voltage drop between electrodes:

$$W = (It)_{actual} \times V = 0.843 \times 10^6 \times \frac{V}{K_c} \text{ kWh/ton}$$

From the above expression it follows that for electrolytic refining to be economically attractive, a great deal of effort should be given to the maintenance of as high a current efficiency and as low a voltage drop as practicable.

Another factor affecting the production rate of electrolytic copper refining is current density. With higher current density, cathodes may be pulled at a younger age and more frequently. On the other hand, the voltage drop across the electrolyte is increased and counter e.m.f. grows, which also means higher costs of power, for the power cost varies directly as the square of the current density. Increased counter e.m.f. has to be made up for by increasing the rate of circulation of the electrolyte which may result in the stirring up of the slime and the contamination of the cathode.

Therefore, a balance has to be struck between these conflicting factors in choosing what may be called the optimum current density. It mainly depends on the composition of anode copper and usually lies within the following limits:

Copper content of anodes, per cent	Optimum current density, A/sq m
98-99	100-120
99.5-99.8	200-400

Anodes and starting sheets are placed into an electrolytic tank by means of an overhead crane. The anodes are left in the tank for 25 to 30 days until they are fully dissolved, depending on their weight and the refining conditions. Average anode copper produces about 15 per cent of its weight of scrap. The scrap anodes are drawn from the tank, washed and sent back to the anode furnace for remelting.

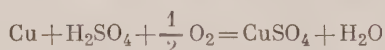
The slime produced by the dissolution of the anodes settles to the bottom of the tank, while some of it remains suspended in the electrolyte. At the end of the run, the accumulated slime is flushed into a launder which takes it to a slime tank where coarse pieces of metallic copper are removed from it, and the slime is pumped for the recovery of the precious metals contained. The composition of the slime depends on that of the anodes (see Table 18).

Table 18

Approximate Composition of Slime
(per cent)

Slime	Cu	Pb	Bi	Sb	As	Ag	Au	Se	Te
Settled	14.3	2.4	0.5	5.5	2.7	35.0	0.6	5.7	2.7
Suspended	0.6	2.8	0.5	48.5	17.8	0.04	—	—	—

The principal values of the slime are gold, silver, selenium and tellurium. The first to be removed is copper. The slime is continually stirred and blown with air and treated with a hot solution of sulphuric acid. The copper of the slime dissolves according to the reaction



The residue is calcined to drive off the selenium dioxide into a dross and is then melted to produce the metal doré (an alloy of gold and silver) and a tellurium-bearing slag. The dross is treated for removal of the selenium, and the slag for the recovery of the tellurium. By another method, after the copper has been recovered, the slime is roasted with an addition of sodium bicarbonate. The selenium and the tellurium pass into the sinter and, upon leaching the sinter with water, into an aqueous solution. The residue is melted to produce doré.

The electrolyte is continually fed to each tank from a common line connected to a pressure tank. On its way to the tanks, the electrolyte is steam-heated to 55-60°C. The electrolyte enters a tank at one end and leaves it at the opposite end. The rate of circulation is so chosen that the whole solution in a tank is fully changed every three or four hours.

The copper produced on the starting sheets forms a dense deposit. With time, however, the rate of deposition across a sheet is upset, and irregularities appear on its surface. These irregularities, or nodules, grow faster on account of a lower resistance between anode and starting sheet at that place. The uneven and porous deposit

will entrap more electrolyte and slime; besides, the nodules may cause short circuits in the tank. Their formation is usually prevented by adding some surface-active materials, such as joiner's glue, gelatine, tannin or wood-pulp wastes. Encouraging results have been obtained by adding a combination of gelatine and thiourea. Their consumption ranges from a few tenths of a gram to several tens of grams per ton of copper.

The cathodes are drawn every 5 to 12 days. A longer run offers no advantages due to the formation of nodules causing short circuits which in turn reduce current efficiency.

The cathodes are removed by an overhead crane and taken to a wash box where they are thoroughly washed by a spray of hot water. Then they may be either fire-refined in reverberatories similar to those for smelting ore, or in induction electric furnaces. Sometimes, cathodes may be shipped without refining.

During a run, it is important to go over the tanks daily, to inspect them for short circuits, cleanliness of the contacts, electrolyte temperature and circulation, and voltage.

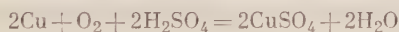
At modern copper smelteries the current efficiency may be as high as 98 per cent and the energy consumption per ton of cathode copper ranges between 200 and 300 kWh.

In the past, direct current for copper electrolytic cells was supplied by motor-generator sets which were more economical than mercury-arc (or mercury-vapour) rectifiers in view of the low voltages (150 to 300 volts) involved. At present, use is being made of silicon rectifiers delivering a current of up to 13 kiloamperes. As a result, the cost of converter stations has been cut down by 50 to 60 per cent.

Automatic monitoring and control of the composition, temperature and rate of circulation of the electrolyte has also added to the efficiency of the process. The loss of heat from the surface of the bath is controlled by covering it with plastic floats and films or organic foams.

Electrolyte Purification. Electrolyte purification is necessitated by the accumulation of impurities and excess copper in it.

Some of the copper present in the electrolyte is dissolved chemically with the participation of atmospheric oxygen:



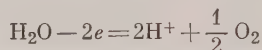
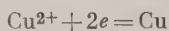
Besides, the anodes contain cuprous oxide which is partly dissolved by sulphuric acid:



The copper passing into the electrolyte in such a case is 0.5 to 1 per cent greater than the amount deposited at the cathode.

The copper sulphate accumulating in the electrolyte may crystallise out at the anodes.

Where the content of impurities is negligible and the purpose of purification is solely the recovery of excess copper, this is done by the use of insoluble lead-anode tanks. The copper in the electrolyte is then deposited at the cathodes, while oxygen evolves at the lead anodes:



The purified solution contains free sulphuric acid and may be returned to the tank room. The voltage necessary for the purification of the electrolyte in insoluble-anode tanks is about 2.5 V. The power consumption is approximately ten times greater than in tanks using soluble anodes.

Where it is desired not only to reduce the amount of copper in the electrolyte but also to remove the impurities with the recovery of the sulphuric acid, the insoluble-anode-tank method is less attractive. By this method the impurities can be completely removed only after all copper has been removed from the electrolyte; the copper precipitated from the depleted solution is contaminated and porous; and the cost of further treatment increases prohibitively.

Instead, use is made of a method based on the manufacture of bluestone. By this method, the electrolyte is heated with hot air and passed through towers filled with shot copper until the free acid is brought down to a negligible proportion. The hot solution is then sent to crystallising tanks where the copper sulphate is allowed to crystallise out into $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The mother liquor is again concentrated with steam coils and allowed to crystallise to produce an additional amount of bluestone. Some manufacturers use vacuum apparatus for the purpose.

Use is often made of a combination of the two methods, one part of the electrolyte to be purified being treated by the insoluble-anode method and returned to the tank room, and the other part is treated for the manufacture of bluestone. The final mother liquor is again electrolytically treated for copper and evaporated to crystallise out nickel sulphate, as nickel always accumulates in the electrolyte.

Chapter VII

THE METALLURGY OF NICKEL

57. General

Nickel is a strong and, at the same time, ductile metal. As distinct from other heavy non-ferrous metals, it is ferromagnetic. Its specific gravity is 8.9; it melts at 1455° and boils at 3075°C . Nickel is face-centred cubic. Its ability to form binary and ternary alloys with many other metals makes nickel an important constituent of more than 3000 alloys used principally for resistance to corrosion and heat.

Chemically, nickel is similar to iron and cobalt, being in the same group of the Periodic System, and is primarily divalent. A few relatively unstable compounds are known in which it is trivalent. Nickel dissolves in acids, producing hydrogen and ions Ni^{2+} , but does not react with alkali.

When oxidised in air, nickel forms nickelous oxide similar to FeO but more readily reducible to metallic form. The higher oxides of nickel are unstable at elevated temperature.

Nickel was isolated by Cronstedt in 1751. Its commercial value had not been however recognised until the last quarter of the 19th century. Its first uses were mainly in armaments and ammunition and later as an alloying agent in alloys of importance to engineering.

Nickel-alloyed steels are ductile and malleable. Additions of chromium make them perfect for structural applications, while high-alloy metals possess outstanding resistance to corrosion, acids and heat. The greater proportion of the nickel produced goes to make alloy steels and a variety of nickel-containing iron alloys, especially magnetic alloys having high magnetic permeability, coercive force and induction. Heat-resistant alloys of nickel, iron and chromium are made into electric heaters and thermocouples.

Another important group of alloys are those of nickel and copper (Monel metals), nickel, copper and zinc (German or nickel silver), in which nickel runs anywhere from 5 to 35 per cent and zinc from 13 to 45 per cent. Monel metals are used where high strength, pressure tightness, high resistance to corrosion and wear are essential (marine, chemical, power, electrical and oil-refinery equipment). German silver can be easily hammered, rolled, stamped and drawn into medical instruments, ribbons and bands, and wire.

Pure nickel has found a broad field of application in instrument-making, vacuum-tube manufacture, and alkaline storage batteries.

Nickel sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, finds use in the manufacture of alkali storage batteries, nickel plating, and as a catalyst.

58. Sources of Nickel

In nature, nickel occurs as sulphides and silicates. Accordingly the sources for its production are sulphide and silicate ores.

Sulphide ores. The principal nickel-carrying material in sulphide nickel ores is pentlandite $[(\text{Ni}, \text{Fe})_9\text{S}_8]$ and, though less, nickel solid solution in pyrrhotite. The other nickel-bearing minerals are of less importance. The nickel in sulphide ores is usually accompanied by copper (mainly as chalcopyrite), cobalt and the platinum-group metals—platinum, osmium, iridium, rhodium, ruthenium and palladium.

An ordinary sulphide ore will carry 0.3-5.5 per cent nickel, 0.6-2.5 per cent copper, and up to 0.2 per cent cobalt. For their high copper content, these ores are often termed copper-nickel.

The gangue of sulphide ores consists of pyrrhotite, magnetite and silicates of iron, aluminium and magnesium.

Like copper ores, nickel ores are classed into massive, pyritic and impregnation, the latter being sulphides disseminated in basic and ultra-basic rocks.

Sulphide ores are subjected to magnetic separation, collective flotation to reject rock and float a sulphide concentrate containing the bulk of the nickel and copper, and differential flotation to produce a nickel concentrate and a copper concentrate. Sometimes it may prove impossible to separate the copper from the nickel due to the intergrowth of the minerals. While copper concentrates are fairly low in nickel, nickel concentrates carry relatively much copper.

In practice, differential flotation is omitted, as the subsequent metallurgical treatment will inevitably separate the two metals.

Silicate (oxide) ores. Oxide nickel ores result from the breakdown of nickel-bearing basic rocks due to weathering. The principal nickel mineral is garnierite, a complex hydrated nickel-magnesium silicate in which the nickel and magnesium contents vary appreciably ($n\text{NiSiO}_3 \cdot m\text{MgSiO}_3 \cdot \text{H}_2\text{O}$). Little copper, if at all, occurs in oxide ores. Cobalt usually occurs in oxide form, associated with manganese minerals. The nickel content of oxide ores (dry weight) is 0.9-1.5 per cent, and the cobalt content up to 0.15 per cent.

The gangue of oxide ores consists of hydrated iron oxides, aluminosilicates, quartz and talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$). This gangue is difficult to slag in nickel smelting owing to the formation of refractory and sticky slags high in MgO .

Oxide nickel ores are distinguished by earthy structure, weak lumps and appreciable hygroscopicity.

No commercial methods for dressing oxide nickel ores have been worked out yet, and they are sent for metallurgical treatment directly.

An approximate analysis of nickel ores is given in Table 19.

Table 19

Approximate Composition of Sulphide and Oxide Nickel Ores
(per cent)

Ore	Ni	Cu	Fe	S	SiO ₂	CaO	Al ₂ O ₃	MgO
Oxide	1.6	None	12	0.01	34	1.5	—	5.1
	0.9	None	14	Traces	42	0.1	1	22.0
Sulphide	2.5	1.1	34	21.0	22	1.9	6	2.0
	5.6	1.8	45	28.0	10	7.0	4	9.0
	0.5	0.8	52	28.0	2	—	—	25.0

59. A General Outline of the Processes

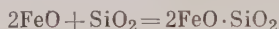
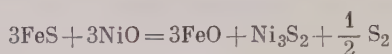
Oxide ores. The main difficulty in extracting the nickel from oxide ores is in its separation from the iron. Attempts to reduce it by smelting while the iron is withdrawn into slag have shown that only some of the iron passes into the slag, the greater proportion of it entering a ferro-nickel alloy; the separation of the iron from the latter is very expensive. Though nickel is predominantly used in special steels, its production as a random ferro-nickel alloy (known as fonte) is hardly acceptable, for it also contains cobalt, manganese, chromium and other impurities in uncontrollable quantities.

Alternatively, a process was for some time used by which the nickel was reduced at low temperatures, producing ferro-nickel alloy. Though less iron was reduced by this method, it fell into disfavour because of the difficulty of recovering the cobalt.

The present treatment is based on the production of a matte by adding suitable fluxes and sulphur-bearing material of some kind, since the oxide ores carry no sulphur of their own. Gypsum is the usual source of the sulphur, though pyrite may also be used, especially produced locally and free from copper and precious metals.

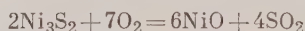
Due to the different affinity of iron and nickel for oxygen and sulphur, smelting produces a nickel sulphide matte which is an

alloy of Ni_3S_2 and FeS , while the bulk of the iron is slagged:



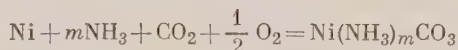
The resultant matte containing up to 60 per cent Fe is then bessemerised while liquid in a converter, a siliceous flux being added to slag off the iron oxide being formed. The product from the converter is practically free from iron. The converter slag is rich in nickel and is usually re-treated in smelting or for cobalt.

The "converter" or "Bessemer" matte is next ground and roasted till free from sulphur, giving practically pure nickel oxide:



The nickel oxide is mixed with a low-sulphur reducing agent, which may be oil coke, and briquetted into either "rondelles" or cubes. The reduction to metallic nickel is carried out in electrical retorts at 1500°C . Fig. 91 shows a flow-sheet of the process.

There also exist hydrometallurgical processes of nickel extraction. One of them has originated in Cuba. After grinding, the ore is subjected to selective reduction in multi-hearth mechanical roasters by producer gas at a temperature well below fusion (600 – 700°C). This reduces the nickel and cobalt to metallic form and the iron to ferrous oxide. Then the charge is leached with ammonia in the presence of carbon dioxide and atmospheric oxygen. The nickel forms carbonatoamines soluble in water according to the reaction:



When the rock has been rejected by thickening and filtering, the solution is treated with live steam. The excess of ammonia is removed, and the solution is hydrolysed, the basic nickel carbonates being precipitated:



The precipitate is ignited in tubular kilns, forming nickel oxide NiO which contains some CoO , while the gases NH_3 and CO_2 are absorbed by water and returned to the leaching tank. The nickel oxide is agglomerated on sintering machines, and the sinter is shipped to steel works.

Another hydrometallurgical process, also of Cuban origin, consists in treating oxide ore with sulphuric acid at 240 – 260°C , with the cobalt and nickel passing into solution. The solution is then thickened, the precipitate washed, the solution purified, and the

cobalt and nickel thrown down as sulphides. The sulphides are then treated for the removal of the metals as described in Sec. 61.

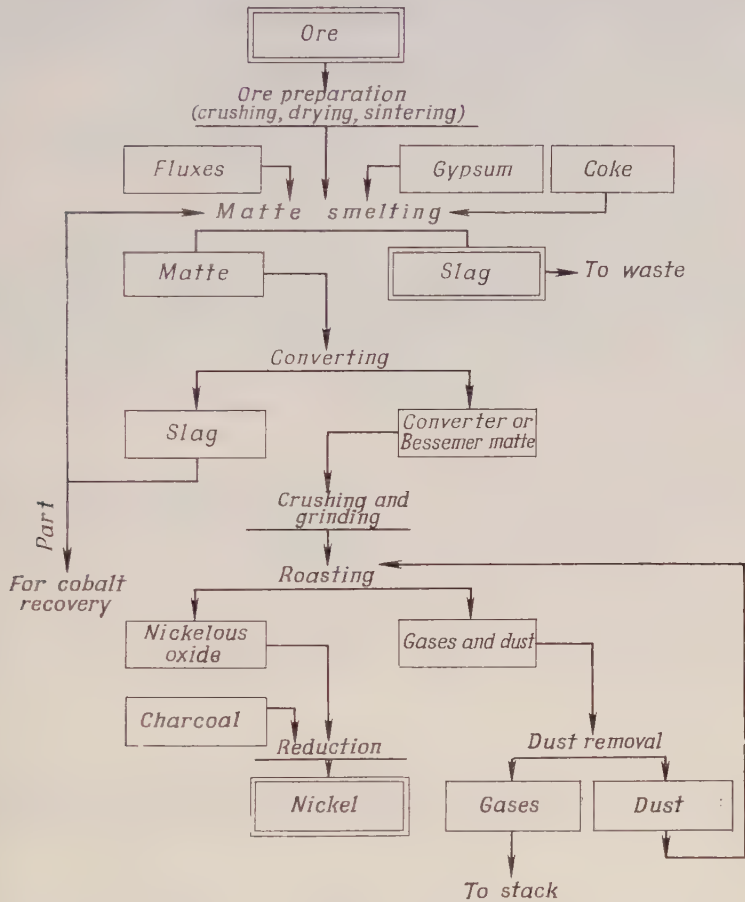


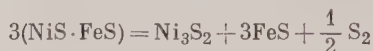
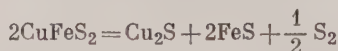
Fig. 91. Flow-sheet for nickel smelting from oxide ores

Sulphide ores. Sulphide nickel ores are mainly treated by pyrometallurgical methods, although hydrometallurgical processes are also known.

Pyrometallurgy of sulphide ores. Ores assaying over 4-5 per cent copper and nickel are considered rich and they are smelted without any preparation. Lean ores are subjected to magnetic separation or flotation.

The ores and the concentrates contain the same minerals. Therefore, the same methods of metallurgical treatment apply.

As the ore is heated to 400-600°C, which is well below fusion, the chalcopyrite and nickel-bearing sulphides are decomposed:



The composite conglomerate of minerals is thus turned into a mixture of simple sulphides Ni_3S_2 , Cu_2S and FeS . At the temperature necessary for melting the slag which consists of gangue oxides and fluxes, the sulphides of copper, nickel and iron are free to dissolve in one another, forming a copper-nickel matte which separates from the molten slag owing to a greater specific gravity.

Where part of the sulphur has been oxidised in smelting or roasting, the distribution of copper, nickel and iron between the matte and the slag will above all be governed by their affinity for oxygen and sulphur.

Under smelting conditions, the affinity for sulphur, which determines whether or not a given metal will enter the matte, grows progressively weaker from the copper to the nickel and the iron, while their affinity for oxygen changes in reverse order. If too little sulphur is present in the charge, first the copper then the nickel and at last some of the iron will pass into the matte. The amount of iron passing into the matte gives a measure of how fully the copper and nickel have been sulphurised, although too much iron in the matte impairs its grade. Still, in smelting either an ore or a concentrate, it is not sought to slag all iron. Some of it is left in the matte for the complete withdrawal of the nickel into the matte.

The molten matte is then bessemerised in a converter for the further removal of iron which is slagged by quartz. The resulting converter matte is an alloy of sulphides of copper and nickel containing 1 to 3 per cent iron. The converter slag is usually added to a fresh charge of concentrate or ore for smelting. Sometimes it may be sent to be treated for the recovery of cobalt. Since cobalt stands midway between nickel and iron in affinity for sulphur and oxygen, some of it is slagged together with the iron. What precious metals are contained in the furnace matte fully pass into the converter matte.

Fig. 92 shows a flow-sheet of the process.

There are several methods for the separation of nickel, copper and precious metals from the converter matte, which are described elsewhere in the book.

Rich copper-nickel ores in large lumps are smelted in blast furnaces unless their gangue is too high melting. In some cases, ores

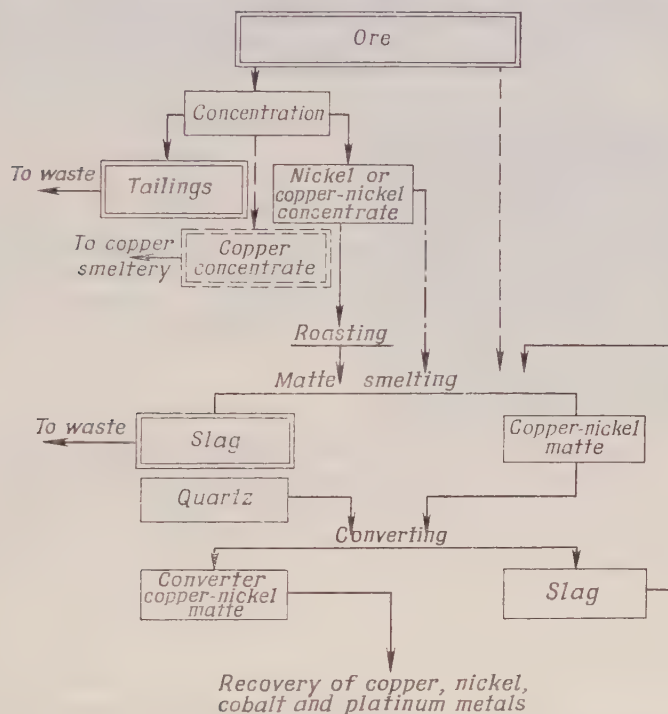


Fig. 92. Flow-sheet for nickel smelting from sulphide copper-nickel ores

high in magnesium oxide and other high-melting constituents have to be smelted in electric furnaces.

Flotation concentrates and the fines of rich ores are smelted in reverberatory or electric furnaces. If the sulphur content is too high, preliminary roasting is resorted to.

The selection of a smelting method depends to a great extent on the composition of the source materials and the prevailing economic factors, notably the availability of a given fuel or the cost of electricity.

Hydrometallurgy of sulphide ores. The crushed ore or the concentrate is leached with an ammonia solution in an autoclave under

a pressure of about 7 atm (gauge). The copper, nickel and cobalt pass into solution as complex ammonites according to the reaction:



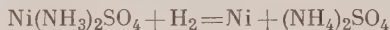
The oxidation of the sulphides generates much heat which is withdrawn by coolers so as to maintain the temperature in the autoclave at 77-80°C. The sulphur in the concentrate is oxidised to $\text{S}_2\text{O}_3^{2-}$, $\text{S}_3\text{O}_6^{2-}$ and SO_4^{2-} , while the iron is precipitated as ferric hydroxide and basic sulphates.

The filtered solution is boiled to precipitate the copper according to the reaction:



The copper remaining in solution is then precipitated by hydrogen sulphide. Next the solution containing nickel and cobalt is treated in the autoclave with hydrogen under a pressure of 15 atm (abs) and at temperatures from 175 to 225°C.

The nickel is precipitated first:



forming particles of elemental nickel measuring 50 to 80 microns across. The nickel residue is filtered out, and the cobalt is precipitated in a similar way, forming a powder which contains 98.6 per cent Co and 0.15 per cent Ni. The precipitation is accelerated by adding seeds to the solutions.

60. Commercial Processes for Oxide Nickel Ores

Though feasible, the smelting of oxide nickel ores in reverberatories has not found any appreciable application, while blast-furnace smelting is employed by a number of manufacturers.

Being soft and loose, oxide ores would disintegrate causing trouble in the blast furnace. Therefore, they are agglomerated before use. One method is to press the ore into briquettes which may be of cylindrical, oval or any other form, weighing 0.2 to 0.3 kg. The binder is the clay of the gangue. Prior to briquetting the ore is ground and dried, and gypsum or pyrite may be added as flux. This improves the homogeneity of the charge and has a wholesome effect on the subsequent smelting.

Briquettes are pressed in a roll and other types of presses (Fig. 93). Unfortunately, briquetting has its drawbacks, one of them being that briquettes may disintegrate in the furnace to form fines which adversely affect the run of the furnace. Another drawback is that briquettes are almost impermeable to gases.

Sintering is a more sophisticated method of agglomeration pioneered in the metallurgy of nickel in the Soviet Union.

Oxide nickel ores are sintered on the machines described earlier. The material to be sintered consists of ore, coke breeze, flue dust, and revert. The ore is first ground to 15-25 mm across in hammer mills. No drying is usually required prior to sintering. The resultant sinter is a lumpy porous mass. The porosity, gas permeability and large reacting surface of the sinter put it high above briquettes.

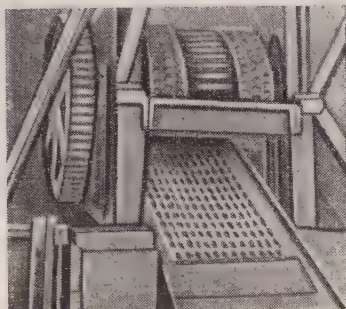


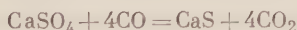
Fig. 93. Roll-type briquetting press

Sintering has increased the daily output of blast furnaces and reduced fuel consumption. Fuel consumption in sintering is 9 to 12 per cent of the charge weight. The output of sintering machines agglomerating oxide nickel ores is 25 to 30 tons per square metre of machine belt per 24 hours. The gases produced in sintering and carrying 0.2 to 0.3 gram of dust per cu m are scrubbed in cyclones.

The sinter is then sized on a screen with bars spaced 20 mm apart, and the fines (20-40 per cent by weight) are returned for resintering.

During smelting, the temperature in the tuyere zone is 1450-1500°C, while at the top the temperature is 300-500°C. The entire column of burden (sinter, pyrite or gypsum, flux and coke) is in a reducing atmosphere, for the gases above the tuyere zone carry up to 35 per cent CO and the top gases 12-16 per cent CO.

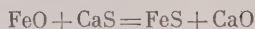
The high temperature and the reducing atmosphere serve together to rapidly reduce the higher iron oxides to FeO and even to Fe, while some of the calcium sulphate (on the surface) is reduced to CaS:



At this stage, not all of the nickel is reduced as its content in the charge is low. Besides, the nickel compounds in the sinter or briquettes are surrounded by the waste rock which hampers free access to them for the reducing gases.

Smelting begins with the formation of low-melting mixtures $\text{FeO-SiO}_2\text{-CaO}$, i.e., at $1050\text{-}1150^\circ\text{C}$. The nickel silicates, ferrous oxide, iron sulphide and calcium sulphide are dissolved in the molten slag which flows down.

In the molten slag, the iron and nickel are sulphurised by the calcium sulphide, and the nickel additionally by the iron sulphide, forming a molten matte consisting of Ni_3S_2 and FeS :



The furnace matte produced from oxide nickel ores is an alloy of sulphides Ni_3S_2 and FeS containing dissolved free iron and nickel. The relative amount of the sulphide and metallic parts of the matte depends on the ratio of the rates at which the metals are sulphurised and reduced in smelting.

When it is produced, the sulphide alloy facilitates the further reduction of the iron and nickel in the slag by the carbon monoxide of the furnace gases and the solid carbon of the coke, as these metals dissolve readily in the nickel matte:

$$(\text{MO}) + \text{CO} = [\text{M}] + \text{CO}_2$$

$$K = \frac{p_{\text{CO}}(\text{MO})}{p_{\text{CO}_2}[\text{M}]}, \frac{p_{\text{CO}}}{p_{\text{CO}_2}} = K \frac{[\text{M}]}{(\text{MO})}$$

The above relation does not give an accurate quantitative measure of the reactions, because it is based on concentrations and not on activities. Still, it gives sufficient ground for stating that the partial equilibrium pressure of the CO in the reduction of iron and nickel from the slag will decrease with decreasing concentration of the metal dissolved in the matte; the presence of solvent makes it easier for a metal oxide to be reduced; the metals are reduced from the slag increasingly easier as the concentration of their oxides in the slag increases.

If the matte saturated with dissolved free metals is allowed to cool, crystals of ferro-nickel, which is a solid solution of nickel and iron, separate out. This may occur when the matte descends from the tuyere zone into the hearth where the temperature is lower. Gradually, the bottom and walls of the hearth are covered with ferro-nickel, the space is reduced, and the normal run is upset.

Referring to the constitution diagram of the system Ni-Fe-S (Fig. 94), the compositions of all practical mattes are bounded by a parallelogram. From the isotherms of the diagram it follows that

the point of crystallisation decreases with increasing sulphur content in the melt. This implies that for the separation of ferro-nickel to be prevented, mattes should be obtained in which the sulphide part is greater than the metallic part.

This purpose is served by pyrite which speeds up sulphurisation. When enough pyrite is added to the charge, very little, if any, ferro-nickel is formed, but the excess of iron sulphide down-grades the matte. An excess of gypsum has little effect on the composition

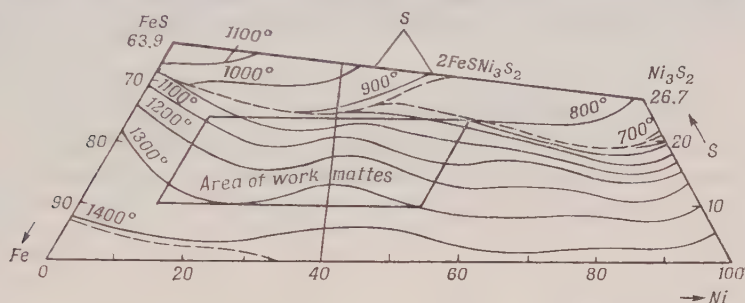


Fig. 94. Constitution diagram of the system Ni-Fe-S

of the matte. This is because the matte is produced with the participation of only the calcium sulphide dissolved in the slag. The excess of CaS is oxidised at the bottom of the furnace and proves useless.

Soviet blast furnaces for nickel smelting from oxide ores take into account the special features of the process.

For one thing, the slag and the matte cannot be separated in the settler, since it is not heated, and it would be quickly covered by ferro-nickel crystals. Instead, the separation of the slag and the matte is effected at the bottom of the furnace, called the crucible.

The crucible is made up of steel plates on a cast-iron soleplate, lined with fireclay and magnesite brick, and ironed with I-beams and channels.

Matte is tapped intermittently, while the slag is allowed to flow off continuously. The slag spout is located 500-600 mm above the matte hole which discharges into a changeable settler for additional separation.

The furnace walls are water-jacketed (see the chapter on copper smelting). As more air is required for smelting, the tuyeres are of the slot type.

The charging mechanism of the furnace is similar to that of a copper-smelting furnace. The furnace is 15 m long, 6 m high, and 1.6 m wide at the tuyeres.

The actual smelting practice differs in detail from plant to plant and depends on prevailing conditions.

The furnace charge usually consists of sinter and flux in lumps measuring 25 to 70 mm across. The flux usually is limestone.

As much as 75 to 80 per cent nickel is withdrawn into the matte. The daily output is 26-28 tons per square metre of tuyere area when working with briquettes, and 30-33 tons per square metre when working with sintered materials. The coke consumption is 32-35 and 22-25 per cent of the weight of the ore, respectively.

The following table gives the composition of the matte.

Table 20

Approximate Composition of Nickel and Nickel-copper Mattes
(per cent)

Product of smelting	Ni	Cu	Fe	S
Furnace nickel matte	16-20	0.1-0.2	54-60	18-20
Converter nickel matte	77.8	Up to 1.0	0.3	22.1
Furnace copper-nickel matte	6.6-11.0	3.00-9.00	54-56	22.0-27.0
Converter copper-nickel matte	41-48	28.00-41.00	0.6-2.6	17.0-20.0

The slag contains 42-44 per cent SiO_2 and about 50 per cent $\text{FeO} + \text{CaO} + \text{MgO}$. The magnesium oxide present in the ore makes it possible to reduce the addition of limestone, and the aggregate content of CaO and MgO in the slag should not exceed 34-35 per cent. The slags of nickel smelting may be fabricated into road stone and mineral wool.

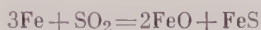
The top gases carry off with them 4 or 5 per cent of the charge (by weight) as dust which is trapped in settling chambers and cyclones and returned for sintering. The gases are usually discharged into the stack, though with a hermetically sealed bell-and-hopper they could be used as fuel.

Nickel matte converting. Nickel matte is bessemerised in converters similar to those used for copper converting.

The bessemerising of nickel matte is characterised by two reactions—the oxidation and the slagging of the iron and iron sulphide dissolved in the matte:

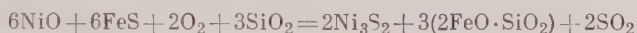


Weight for weight of iron, the latter reaction takes three times more air for slagging than the former. Moreover, the former reaction proceeds at a far higher rate. Furthermore, the iron may be oxidised by sulphur dioxide:



Experience shows that the iron sulphide begins to burn out only after the bulk of elemental iron has been slagged.

The nickel is not oxidised until after all iron in the matte is slagged, for if nickel oxide were formed, it would be immediately resulphurised:

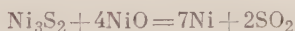


The matte is charged into the converter a ladle (i.e., 4 to 10 tons) at a time, after which quartz is added, and the matte blown. The procedure is repeated until the molten metal is built up the full capacity of the converter. The slag flushed from the converter is usually low in nickel and cobalt on account that the matte in the converter still contains much iron. The duration of a blow increases from 15 to 45 minutes as the matte in the converter is accumulated. This is because the ratio of free iron to iron sulphide decreases.

During the hot run when the metallic iron is slagged at a high rate, cold charges of ferro-nickel, solid matte and other nickel-bearing revert are introduced into the converter.

When enough matte low in iron has been accumulated in the converter, it is bessemerised. After the converting, the slag is tapped first, and the converter matte is cast into moulds.

No amount of further blowing can turn the converter nickel matte into pure nickel. The reaction between the nickel sulphide and the nickel oxide:



can take place only at very elevated temperatures hardly attainable in a converter even with additional heating. The equilibrium pressure of SO_2 for this reaction is as follows:

Temperature,	deg. C	90	1100	1300	1500
$K_{eq} = p_{\text{SO}_2}$,	atm	$10^{-5.5}$	$10^{-2.6}$	10^{-1}	$10^{0.8}$

Converter slag contains 25-30 per cent SiO_2 , 42-48 per cent Fe and about 1.5 per cent Ni. The cobalt content is not over 0.2 per cent in the bulk of slag, and up to 1.5 per cent in the closing skims.

The dust carried off by the top gases assays 15-20 per cent nickel; it is recovered in settling chambers and returned to the converter during the next blow.

The capacity of nickel converters (in terms of copper) is anywhere from 20 to 40 tons, with a single run lasting for 8 to 12 hours, of which time up to 85 per cent is taken up by the blow.

Refining of the Converter Nickel Matte. The converter matte is roasted "dead", i.e., until all of the sulphur is eliminated, or it will contaminate the pure nickel separated.

The presence of a sulphate in the calcine is as intolerable as that of a sulphide: the sulphate will inevitably be reduced to Ni_3S_2 . The formation of the sulphate is prevented by raising the roasting temperature to 900-1000°C on account that under such conditions NiSO_4 has a high dissociation pressure and will be completely decomposed. The roasting operation cannot however be started at 900°C for the reason that the matte will melt.

As a way out, the matte is roasted twice. The first roasting is conducted in mechanical multiple-hearth roasters where the material is gradually raised to 850-900°C while being continually rabbled. The first roasting eliminates 90 to 95 per cent of the sulphur in the matte.

The partly sintered product of the first roasting is cooled, ground and again roasted in rotary kilns at 1400° till it contains 0.01-0.02 per cent sulphur.

The multiple-hearth roasters were described earlier (Chapter VI). Those used in nickel matte refining additionally have two or three fireboxes to burn fuel oil or gas.

The rotary kiln (see Fig. 177) used for the second roasting is a steel cylindrical jacket about 20 m long and 1.6 m in diameter. It makes an angle of 2° with the horizontal and has several rims supported by rollers so that it rotates at about one revolution per minute. The kiln is lined with firebrick. The ends of the jacket fit into hoods of firebrick. The hood at the raised end has a connection with the gas flue and is fitted with a charging device. The lower-end hood incorporates a firebox burning low-ash coal or fuel oil. The products of combustion pass through the kiln and into the upper-end hood. The material is charged and stirred continuously, moving against a stream of hot gases as the kiln is rotated.

The converter matte charged into the twelve-hearth roaster is ground to particles measuring 0.4-0.6 mm. The calcine discharged from the bottom hearth contains 1.5 to 3 per cent sulphur. It is charged into a cooler which is an inclined rotary steel cylinder. If necessary, the tube may be employed for chlorine roasting with which copper is converted to compounds soluble in acid-containing water. This treatment removes what copper may be present in the matte.

From the cooler the calcine is taken to a vibrating screen. The oversize material is then ground in a ball mill and charged into

the kiln together with the calcine that has passed through the screen. After the second roasting, the material goes to the second cooler.

The waste gases from the first and second roasting are cleaned of dust in electrostatic precipitators. The grinding and conveying equipment is made air-tight and a vacuum is maintained inside it to prevent the loss of dust carrying valuable nickel. The gases thus aspirated are cleaned of dust and the latter is returned for roasting.

The twelve-hearth roaster of the first roasting with a total hearth area of 320 sq m treats about 55 tons of matte per 24 hours, consuming 20 to 25 per cent of the charge weight of fuel. About 8-9 per cent of the material is carried off with dust.

The rotary kiln of the size indicated above can well handle the calcine from one twelve-hearth roaster. Fuel consumption is 25-30 per cent of the weight of the calcine. Of late, much headway has been made by the nickel industry in the use of the fluidised-bed technique by which the roasting can be completed in a single stage.

Nickel oxide can be reduced at low temperature (600-700°C). Molten nickel is however required for subsequent operations, and so the reduction is carried out in electric furnaces at a temperature of about 1500°C. The reducing agent is charcoal or oil coke, i.e., carbonaceous materials free from sulphur.

About 40 per cent of the nickel oxide in the converter matte is reduced while the calcine cools in the cooler past the kiln. As a result, considerably less gas is evolved during electric melting and less dust formed.

In the Soviet Union, the electric furnaces used for the purpose are the PHB-5 and the ДСТ-5, both used in steel-melting. Each holds 5 to 8 tons of nickel and operates intermittently, each run lasting 6 to 8 hours.

Limestone is added to the charge to slag off the inevitable though small amounts of impurities and to eliminate all sulphur in the metal. The silica, alumina and other oxides entrained by the nickel oxide due to the wear of the lining in the roaster and the rotary kiln are fluxed to form a small quantity of basic limy slag carrying 0.2 to 0.4 per cent nickel.

The molten bath is skimmed clean; the carbon dissolved in the nickel is oxidised by adding a small quantity of NiO, the metal is cast into moulds or granulated. For granulation, the molten nickel is poured in a thin jet into a basin filled with water which should be stirred to avoid explosions.

61. Commercial Processes for Sulphide Nickel Ores

Pit-run ore is broken up to pieces 200 mm across and screened into a portion passing through a sieve with 50-mm openings and another portion which stays on the same sieve. Part of the gangue is hand-picked, while lumps rich in sulphides are separated magnetically on account that the pyrrhotite usually accompanying pentlandite is magnetic. This treatment is applied both to the "fines" and the "coarse" ore. Sometimes, the "coarse" fraction is again crushed and fed into magnetic separators to recover the magnetic portion.

The flotation of sulphide ores is based on the fact that chalcopyrite floats while iron and nickel sulphides sink.

The products of collective and differential flotation are presented in Table 21.

Table 21

Flotation of Sulphide Nickel Ores

Product	Composition, per cent				
	Ni	Cu	Fe	S	SiO ₂
<i>Collective flotation</i>					
Ore	0.85	1.12	17.4	7.6	39.1
Collective concentrate	3.18	4.48	39.0	28.2	12.1
Tailings	0.065	0.03	10.1	0.3	48.8
<i>Differential flotation</i>					
Ore	2.5	4.0	33.25	19.8	23.1
Copper concentrate	1.5	28.0	48.25	32.2	4.1
Nickel concentrate	9.0	5.0	37.00	25.6	14.6
Tailings	0.2	0.1	19.70	5.0	44.2

The choice of a flotation method depends on the ore to be dressed and local conditions.

Where direct smelting in reverberatories or electric furnaces will not produce a high-grade matte because of the high iron-sulphide content of the ore, it is previously roasted.

The roasting of green sulphide ore takes more time than that of copper concentrate because of the slow oxidation of the sulphur. This is due to the fact that in the ore the sulphur is present predominantly as pyrrhotite (Fe_7S_8); when pyrrhotite is heated, only one-eighth of the sulphur is given up while the decomposition of pyrite (FeS_2) eliminates half the sulphur. In heating, pyrite cracks, which

fact speeds up its oxidation, while pyrrhotite is denser and does not crack in heating.

Concentrates are roasted in a mixture with ground rich ore and the fluxes required for the subsequent smelting. The roasting is conducted either in multiple-hearth roasters or in sintering machines. The heat generated during the roasting comes solely from the combustion of the sulphides, and the temperature rises to 850°C.

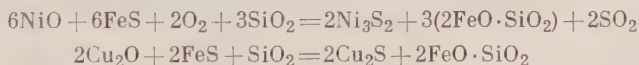
The waste gases from the multiple-hearth roasters are cleaned in electrostatic precipitators and may be used in the manufacture of sulphuric acid. Due to slow oxidation, only 40 to 50 per cent of the sulphur is eliminated. The capacity of a ten-hearth roaster is 150 to 275 tons of charge per 24 hours.

The Smelting of Concentrates and Rich Ores. Concentrates and fine ores with a relatively low-melting gangue requiring little flux are smelted in reverberatory furnaces. Reverberatory smelting is, however, advantageous where fuel is reasonably cheap.

Electric smelting is resorted to where the charge will form high-melting slags, which is true of ores and concentrates high in magnesium oxide. When smelted in fuel-fired furnaces, they require much flux, and the losses of nickel and copper increase. Electric smelting, however, is advantageous only where electricity is not expensive.

The reverberatory smelting of sulphide nickel ores does not materially differ from that of copper ores. The sulphur is eliminated mainly owing to the higher iron oxides. When green ore and concentrates are smelted, some of the sulphur is also eliminated owing to the dissociation of the higher sulphides.

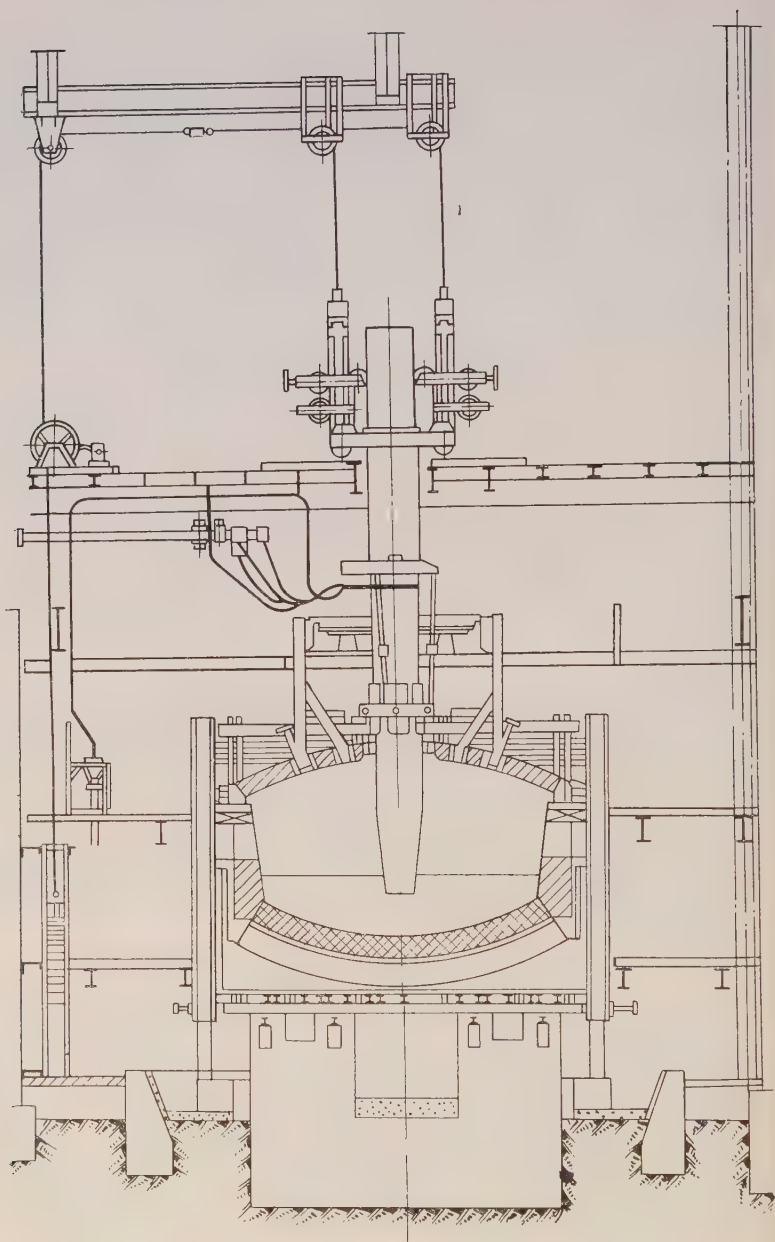
The principal reaction of smelting is the one between the oxides of copper and nickel, on the one hand, and the iron sulphide, on the other. The copper and nickel pass into the matte, and the iron into the slag:



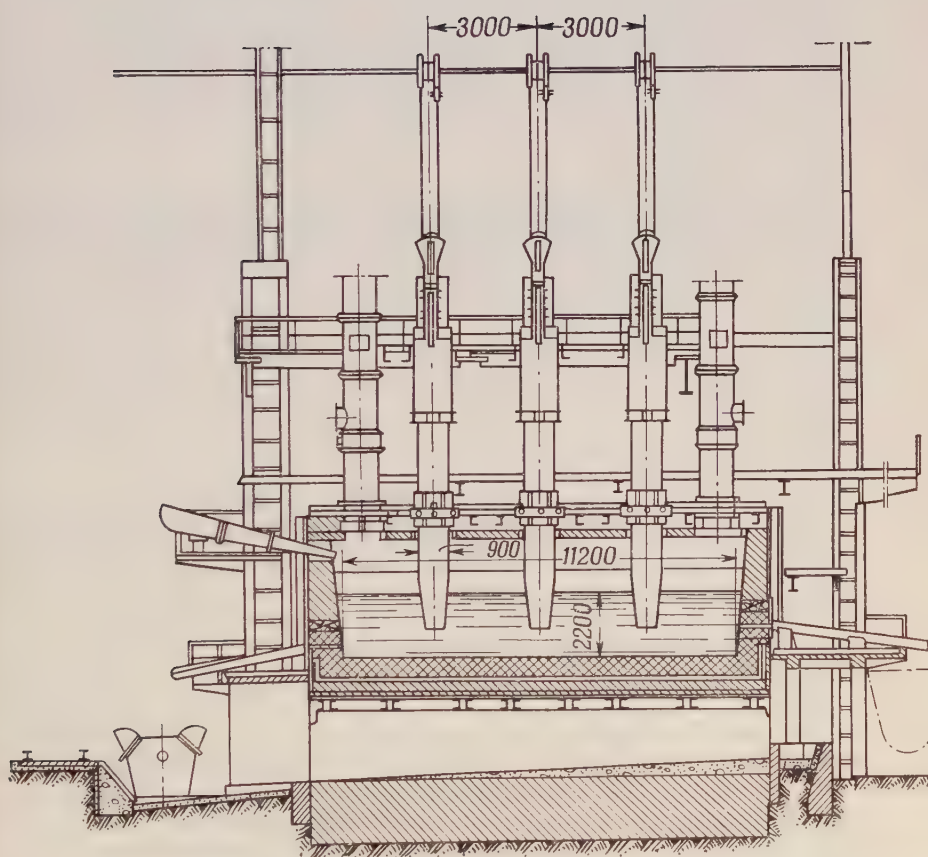
The distribution of the copper, nickel and iron between the matte and the slag depends on their affinity for oxygen and sulphur.

Volsky has suggested to estimate the probability for a metal to change from sulphides to oxides on the basis of the difference in the standard free-energy change, ΔG , for its reactions with oxygen and sulphur. Table 22 presents data on some of the metals.

As the desulphurisation in the smelting furnaces progresses, first some of the iron, then more iron and some of the nickel, next more nickel, and finally the remaining nickel and copper pass into slag. No clear delineation is possible between these stages, as the affinity



◀ Fig 95. Electric furnace for nickel-matte smelting



of a given metal for oxygen or sulphur depends on the concentration (or, rather, activity) of its compounds in the matte and the slag.

Table 22

**Probability of Transformation from Sulphides
to Oxides for Some Metals**

(The difference in standard free-energy change for reactions with oxygen and sulphur, ΔG , kcal/g-atom)
(after Volsky)

Metal	Temperature, deg. C		
	900	1100	1300
Calcium	-23.4	-24.1	-24.7
Manganese	-33.8	-35.1	-36.6
Iron	-27.3	-28.2	-29.0
Zinc	-25.9	-25.7	-25.1
Lead	-17.2	-15.6	-14.3
Nickel	-24.8	-21.0	-16.8
Copper	+3.0	+3.0	+6.7

For the efficient transfer of nickel and copper into the matte, desulphurisation should proceed to a point where only some of the iron will be slagged. No attempt is made in smelting to slag off all iron, since the loss of metal in the slag would be too great.

The reverberatory furnaces used for smelting sulphide nickel ores are similar in construction to those used for copper smelting. Their outputs are also very close to each other. In the case of sulphide nickel ores, the daily output of a reverberatory furnace is 4.5 tons of calcine per square metre of hearth area. The fuel consumption is 11-12 per cent of the weight of the charge.

Electric furnaces are usually rectangular in plan, with a hearth area of 140 sq m (23.6 m long by 6 m wide). Passed into the furnace through the roof are three or six continuous carbon electrodes 900 to 1400 mm in diameter. The tips of the electrodes are dipped into molten slag (Fig. 95) which serves as a resistor. The temperature of the molten bath is maintained automatically by a device which moves the electrodes up or down so as to maintain a preset current. In addition, the temperature may be controlled by varying the supply voltage anywhere between 300 and 500 V, as well as by varying the charging and tapping schedule.

The charge is introduced into the furnace chamber through an opening in the roof near or around the electrode. For better temperature control, the depth of the slag layer is maintained between 1.4 and 1.8 m.

The capacity of electric furnaces is up to 12 tons of charge per square metre of hearth area per 24 hours, and power consumption is 700 to 850 kWh per ton of charge. With less slag produced and less dust lost, as much as 96 per cent of the copper, nickel and precious metals present in the charge is withdrawn into the matte. Modern electric furnaces for nickel smelting are built in ratings from 15 to 35 MW.

Blast-furnace smelting is suitable for coarse ore and sinter, and is advantageous where coke is cheap, its consumption reaching 9-11 per cent of the weight of the charge.

The blast-furnace smelting of sulphide nickel ores is similar to the partial pyritic process in copper smelting. Desulphurisation, however, goes to a lower extent than in copper smelting due to the high pyrrhotite in the charge and the increased coke consumption, and the resultant matte is of lower grade. Thorough ore sizing, coupled with the sintering of fines and concentrates, makes it possible to obtain mattes with an aggregate content of nickel and copper up to 15-25 per cent. Higher grades of matte would be unprofitable to smelt because of the increased metal loss in the slag.

The aggregate content of copper and nickel in the slag does not exceed 0.2-0.4 per cent. Still, due to much slag produced per unit weight of matte, the recovery of copper, nickel and precious metals from the charge reaches 90 per cent only where a high-grade charge is used.

The daily output of blast furnaces ranges within broad limits and depends on the composition of the source materials and their preparation prior to smelting. Thus, for sinter it is higher than for green ore. The average figure is from 70 to 140 tons per square metre of area at the tuyeres per 24 hours.

Table 23

**Approximate Composition of Slags from Oxide
and Sulphide Nickel Ore Smelting**
(per cent)

Smelting	Ni	SiO ₂	FeO	CaO	Cu	Al ₂ O ₃	MgO
Blast-furnace (oxide ores)	0.17	42	17	18	None	6	12
Blast-furnace (sulphide ores)	0.12	39	38	7	0.12	12	3
Reverberatory-furnace (copper-nickel concentrates)	0.20	36	52	3	0.08	6	2
Electric-furnace (sulphide ores)	0.07	45	25	2	0.06	3	25

The composition of blast-furnace slags is presented in Table 23 which also gives the composition of the slag from the smelting of oxide nickel ores.

Bessemerising (Converting) of Copper-nickel Matte. Irrespective of the process employed, the copper-nickel matte is an alloy of sulphides of copper, nickel and iron containing dissolved ferrites, cobalt sulphide and platinum-group metals. On top of all, there also is some amount of dissolved worthless rock. The sulphur content of copper-nickel mattes averages 25 per cent.

The copper-nickel matte is bessemerised solely for the purpose of oxidising and slagging the iron prior to the subsequent treatment of the Bessemer matte. The blow lasts for 24 to 30 hours, depending on the grade of the furnace matte.

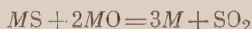
The cobalt passes into the converter slag predominantly at the end of the run. To recover it, the slag is sent for separate treatment.

The current view in the Soviet Union is that it is disadvantageous to recover cobalt matte from Bessemer slag. Instead, it is sought to transfer as much cobalt as practicable into the nickel matte and to recover the cobalt during the subsequent electrolytic refining of the nickel.

This is the reason why at some plants all Bessemer slag is melted on a bed of nickel matte charged into the furnace in advance. The smelting operation is carried out in small electric furnaces and yields barren slag and cobalt-enriched matte.

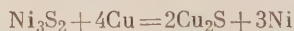
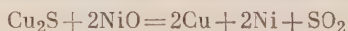
At plants equipped with reverberatory or electric furnaces, molten slag is poured directly into the furnace. In the case of blast furnaces, the slag is cast into moulds, broken up and added to the charge for blast-furnace smelting. Converter slag assays 16-25 per cent SiO_2 and about 65 per cent FeO .

The Bessemer copper-nickel matte is an alloy of copper and nickel sulphides and contains 3-4 per cent Fe and about 20 per cent sulphur. Towards the end of the blow, the copper and nickel oxides begin to react with the sulphides:



for which reason free dissolved nickel and copper are always present in the matte.

The nickel is apparently reduced according to the reactions:

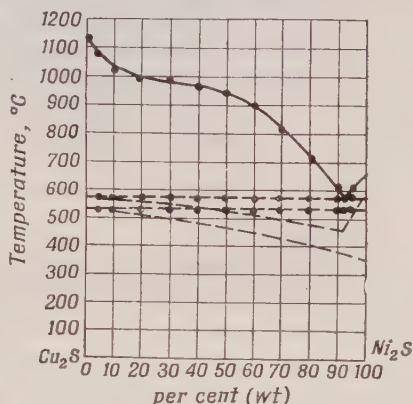


Refining of the Bessemer Copper-nickel Matte. The total content of copper and nickel in Bessemer copper-nickel mattes is 77-78 per

cent. The percentage ratio of the two metals depends on the composition of the source ore. Usually, it ranges between 2 : 1 and 1 : 2.

The Bessemer copper-nickel matte can be easily melted into Monel metal. To this end, the matte is crushed, ground, and roasted dead. The mixture of NiO and CuO thus obtained is then reduced in reverberatory furnaces. The requirements in Monel metal, however, are limited. Furthermore, the platinum-group metals and cobalt contained in the Bessemer matte cannot be recovered. Therefore, the Bessemer matte is more often treated in order to separate pure nickel and copper and to recover the cobalt and precious metals.

Fig. 96. Constitution diagram of the system $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2$ (after Friedrich)



The first stage in such treatment is the separation of the nickel and copper. It is achieved by subjecting the Bessemer matte to controlled cooling, fine grinding, magnetic separation and differential flotation.

In the Soviet Union, this process based on the properties of the system $\text{Ni}_3\text{S}_2-\text{Cu}_2\text{S}$ and the floatability of sulphides has been developed by Maslenitsky. The properties of the system $\text{Ni}_3\text{S}_2-\text{Cu}_2\text{S}$ referred to consist in that when the Bessemer matte is allowed to cool, crystals of Cu_2S are rejected from it (Fig. 96), and at 595°C a ternary eutectic $\text{Cu}_2\text{S}-\text{Ni}_3\text{S}_2-(\text{Ni} + \text{Cu})$ solidifies. The low rate of cooling from 1135 to 595°C promotes the growth of Cu_2S crystals. In the solidified matte, Cu_2S is present as fairly large grains. When ground, the matte is turned into a mixture of particles of Cu_2S , Ni_3S_2 and $\text{Ni} + \text{Cu}$ alloy, easily separable by differential flotation. In practice, the process is handicapped by the presence of metallic alloys in the matte. Fortunately, copper-nickel alloys, as distinct from sulphides, are magnetic and can be withdrawn by magnetic separation. The metallic fraction thus liberated contains precious (platinum-group) metals.

If the bessemerising of nickel matte is stopped at a temperature of not over 1200°C and in the presence of excess quartz, the sulphur content of the matte will be as high as 22 to 25 per cent and the yield of the metallic fraction after the subsequent flotation will be appreciably reduced. Flotation will then yield only two products: copper concentrate and nickel concentrate, the latter carrying the bulk of the platinum-group metals.

Fig. 97 shows a flow-sheet of the process, and Table 24 summarises its performance.

Table 24

**Separation of Copper and Nickel by Differential Flotation
of Bessemer Copper-nickel Matte**
(After Maslensky and Krichevsky)

Product	Content, per cent		Removal, per cent	
	Ni	Cu	Ni	Cu
Source matte	24-25	26-53	—	—
Nickel concentrate	67-68	2-3	95-97	2-4
Copper concentrate	4-6	68-74	3-10	85-90

The nickel concentrate is roasted dead, and the resulting nickel oxide is reduced by carbon in electric furnaces to metal which is cast into anodes and refined electrolytically.

Until recently, the roasting of nickel concentrate in a fluidised bed was handicapped by the low melting point and fineness of the concentrate. At present, the concentrate before roasting is pelletised and agglomerated by sintering. During the roasting operation the depth of the fluidised bed is maintained anywhere between 2.5 and 3.5 m, working with an excess of air ($\alpha = 1.1$). The fines are recycled into nickel-concentrate thickeners, where they are intimately mixed with the concentrate. This method produces fairly large grains of nickel oxide, carrying not over 0.25 per cent sulphur. The rate of operation of a fluidised-bed roaster may be as high as 8 tons/sq m per 24 hours. The recycled fines account for about 20 per cent, and the irrecoverable losses for not over 0.3 per cent.

The copper concentrate is treated in the usual manner, first by bessemerising and then by refining electrolytically.

The Mond Process. This process is applicable to various nickel-bearing materials, including "overblown" Bessemer mattes (containing about 8 per cent sulphur), the magnetic fraction separated

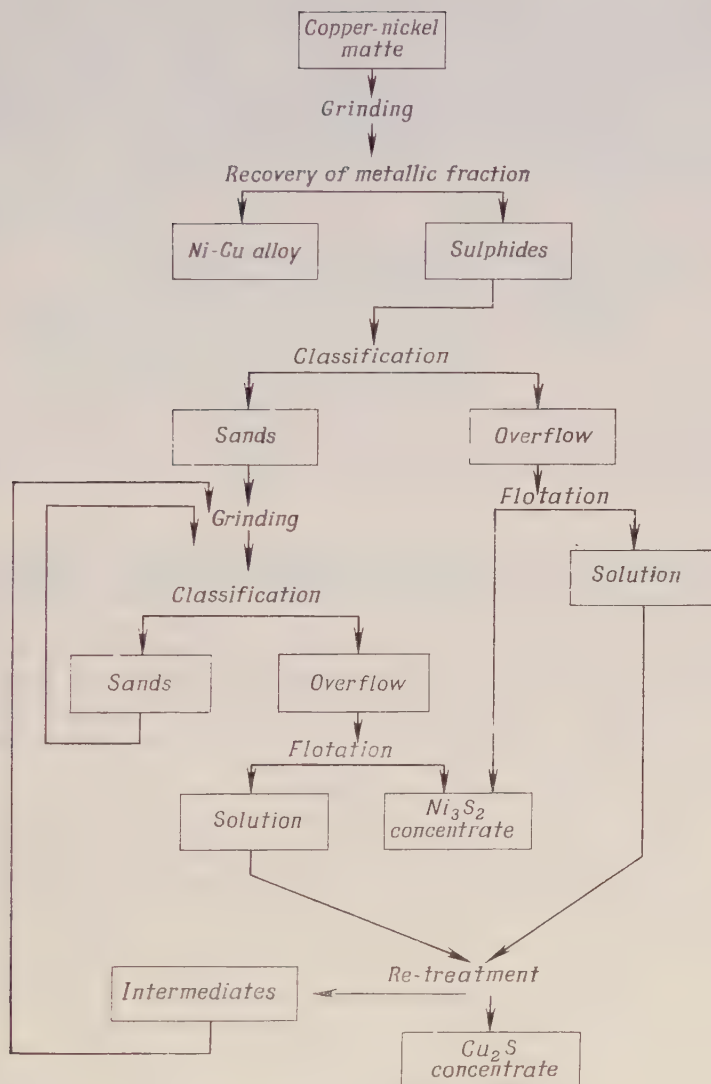


Fig. 97. Flow-sheet for flotation of converter copper-nickel matte

by differential flotation, and the anode slime from the electrolytic operation.

The process is based on the property of nickel, cobalt and iron to combine with carbon monoxide, forming volatile carbonyls whose composition may be generalised by the formula of the type $M(\text{CO})_n$. Table 25 gives an idea of some of the properties of nickel and iron carbonyls.

Table 25

Some Properties of Nickel and Iron Carbonyls

Formula	Temperature, deg. C		
	melting	boiling	decomposition
$\text{Ni}(\text{CO})_4$	-25	43	200
$\text{Fe}(\text{CO})_5$	-20	103	over 200

Cobalt produces carbonyls $\text{Co}(\text{CO})_3$ and $\text{Co}(\text{CO})_4$ only under some pressure, but they decompose easily. Copper does not produce carbonyls.

From the reaction $\text{Ni} + 4\text{CO} = \text{Ni}(\text{CO})_4$ it follows that the formation of nickel carbonyl is accompanied by a sharp reduction (by a factor of four) in the volume of the gases. Consequently, according to Le Chatelier's principle, this reaction can be encouraged by increasing the pressure on the system.

The material crushed to pieces 30-40 mm across is charged into a thick-walled steel cylinder, called the volatiliser, where it is treated with carbon monoxide under a pressure of about 250 atm. The charge is heated to 230-250°C by the heat of the reactions. The gases evolved are passed through a cooler and returned to the volatiliser.

In the cooler, a mixture of liquid carbonyls of nickel, iron and, to a lesser degree, of cobalt is accumulated. The solid residue in the volatiliser contains copper, platinum and impurities; the nickel content in the residue does not exceed 8 per cent. The mixture of liquid carbonyls is then fractionated to separate pure nickel carbonyl. The gaseous nickel carbonyl is next passed through an iron tower, called the decomposer, where it is heated to 320°C to decompose into pure powdered nickel and carbon monoxide which is recirculated. The solid residue in the volatiliser is treated to remove cobalt. Cobalt carbonyl is stable up to 60°C; when it is heated to a higher temperature, it decomposes.

62. Electrolytic Nickel Refining

Electrolytic refining is employed to obtain the highest grades of the metal containing 99.9-99.99 per cent nickel and to recover precious metals, selenium, tellurium and cobalt.

Table 26 gives the composition of the nickel smelted from oxide and sulphide ores prior to refining, and Table 27 of the commercial grades of nickel to a relevant U.S.S.R. State Standard.

Table 26

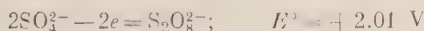
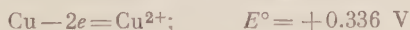
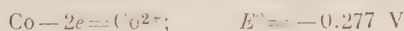
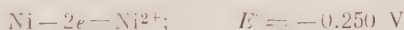
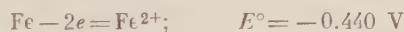
Composition of Nickel Prior to Refining

Ore	Composition, per cent					
	Ni+Co	Co	Fe	Si	C	Cu
Oxide	99.2-99.6	0.4-0.8	0.4-0.8	max. 0.02	max. 0.4	0.004-0.4
Sulphide	93.1-95.6	0.3-0.9	1.3-2.5	0.1-0.3	max. 0.6	2-2.6

A comparison of the two tables will show that the nickel smelted from oxide ores meets, in the main, the requirements of the two lowest grades, while the metal smelted from sulphide ores does not answer the specification of any grade, mainly as far as the iron and copper content is concerned. Besides, the nickel smelted from oxide ores usually does not contain precious metals, while that from sulphide ores always carries platinum-group metals which are valuable enough to warrant their recovery. The above considerations explain why electrolytic refining is primarily applied to the nickel smelted from sulphide ores.

Nickel is electrolysed in a solution of nickel sulphate or a mixture of nickel sulphate and chloride with an addition of some current-conducting agents.

The following electrochemical reactions may be thought of as taking place at the nickel anode:



From a comparison of the values of E° , it seems clear why only nickel, cobalt and some of the copper pass into solution from the

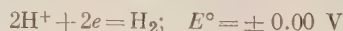
Table 27

Nickel Grades to U.S.S.R. State Standard
(per cent)

Elements	Grade designation				
	H0	H1	H2	H3	H4
Ni + Co, min;	99.99	99.93	99.8	98.6	97.6
including Co, max.	0.005	0.10	0.15	0.7	0.7
Impurities, max.:					
carbon	0.005	0.01	0.02	0.1	0.15
magnesium	0.001	0.001	—	—	—
aluminium	0.001	—	—	—	—
silicon	0.001	0.002	0.002	—	—
phosphorus	0.001	—	—	—	—
sulphur	0.001	0.001	0.003	0.03	0.04
manganese	0.001	—	—	—	—
iron	0.002	0.01	0.04	—	—
copper	0.001	0.02	0.04	0.6	1.0
zinc	0.001	0.001	0.005	—	—
arsenic	0.001	0.001	—	—	—
cadmium	0.0003	0.001	—	—	—
tin	0.0003	0.001	—	—	—
antimony	0.0003	0.001	—	—	—
lead	0.0003	0.001	—	—	—
bismuth	0.0003	0.001	—	—	—
Total impurities, max.	0.01	—	—	—	—

anode while the remaining part of the copper and all platinum-group metals pass into the slime after the anode has been fully dissolved. The potential at the anode is not sufficient for the evolution of oxygen. Yet, some oxygen apparently appears at the anode, thereby passivating it, i.e., slowing down its dissolution. An addition of sodium chloride prevents the passivation of the anode.

At the cathode the same electrochemical reactions must proceed in a reverse order. Accordingly, one should expect that ions Cu^{2+} discharge first, followed by hydrogen:



and finally by nickel and cobalt.

In view of the above sequence of discharges, the cathodes in tanks for the electrolysis of nickel are placed in bags consisting

of wooden frames with fabric sides made of flaxen canvas with an addition of Dacron-type synthetic fibre (Fig. 98). The electrolyte inside the bags is called catholyte and outside them anolyte.

The anolyte contains copper and other impurities continually coming from the dissolving anodes. It is continually withdrawn from the tank and purified. The purified electrolyte is fed into the

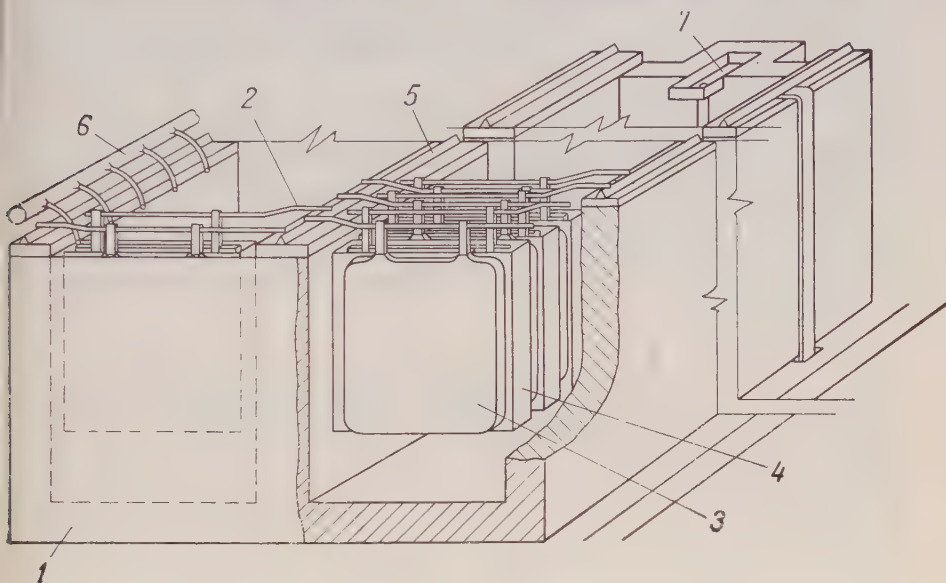


Fig. 98. Electrolytic cell for nickel manufacture:

1—cell; 2—cathode; 3—anode; 4—bag; 5—copper busbar; 6—catholyte into bag;
7—anolyte out

cathode bags at a rate sufficient to maintain a head of about 50 mm above the level in the anode compartment. This is to prevent anolyte containing copper from flowing into the cathode bags and contaminating the nickel. On the other hand, the catholyte is free to seep through the diaphragm and into the anode space.

The copper from anolyte is removed by cementing it with powdered nickel according to the reaction:



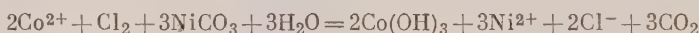
The cementation is carried out either by mixing the anolyte with powdered nickel or by allowing the anolyte to seep through the latter two or three times. As more copper accumulates on the surface of the nickel particles, the rate of the reaction slows down.

Therefore, 1.5 to 3 parts of powdered nickel (by weight) goes to cement one part of copper, leaving as little as 0.5 mg/litre of copper in the foul electrolyte. The temperature of the anolyte during cementation is maintained at 50-70°C. The precipitate of cemented copper which contains some nickel is given further treatment.

The iron is removed by charging nickel carbonate and blowing the solution with compressed air. This first produces ferrous carbonate which is then oxidised by the oxygen of the air and hydrolysed to basic iron salts, such as Fe(OH)CO_3 or Fe(OH)SO_4 , and further to hydroxide at pH 3.6-4.2.

The iron is removed in tanks equipped with pneumatic stirrers similar to those employed in zinc metallurgy. Stirring the solution with nickel carbonate at 60-70°C for two or three hours brings down the iron content to 5-10 mg/litre. Nickel carbonate is prepared by precipitating nickel from a portion of the solution by soda ash.

Cobalt is recovered by acting on the solution simultaneously with gaseous chlorine and nickel carbonate. The cobalt appears in the precipitate:



The precipitate containing 4-6 per cent cobalt oxide is treated to recover some of the nickel and then the cobalt.

The purification of the solution does not of course preclude the discharge of hydrogen ions at the cathode, which fact may reduce the current efficiency of nickel recovery. The evolution of hydrogen is to some extent prevented by its overvoltage on the nickel. The discharge potential of hydrogen ions may be expressed as

$$E_{\text{H}} = \frac{RT}{F} \ln a_{\text{H}} + \eta$$

where E_{H} = potential of hydrogen evolution;

a_{H} = activity of hydrogen ions in solution;

η = overvoltage of hydrogen on nickel.

In order to make E_{H} more negative, a_{H} should be decreased, i.e., the pH of the solution increased. At pH 6, the hydrolysis of nickel sulphate may begin, which would be accompanied by the deposition of basic salts at the cathode, thereby making the metal deposit non-uniform and striated. As a precaution against this occurrence, catholyte is fed at pH 3.5 with an addition of boric acid to stabilise the activity of the hydrogen ions. In order to increase the other component of the potential, i.e., overvoltage, the density of current is increased. The composition of catholyte in nickel electrolysis is given in Table 28.

Prior to purification, anolyte may contain up to 1 g/l Cu, up to 0.25 g/l Fe and 0.25 g/l Co.

Composition of Catholyte
(g/l)

Table 28

Catholyte	Ni	H ₃ BO ₃	Na ₂ SO ₄	NaCl	Residual impurities		
					Cu	Fe	Co
Sulphate	50-60	10	50	3-7	0.002	0.001	0.02
Sulphate-chloride	50-70	4-6	—	50	0.002	0.001	0.02

Electrolytic tanks are built of concrete lined with acid-proof brick or ceramic tile, or use may be made of plastics. A tank usually measures 5.6 m in length, 0.86 m in width, and 1.4 m in depth.

Nickel anodes are cast as rectangular plates 250-300 kg in weight, measuring about 700 mm by 900 mm. Starting sheets are 50 mm wider than anodes and are made through the electrolysis of purified solution in separate tanks on blanks of stainless steel or of titanium.

Usually, a tank has 33 cathodes and 34 anodes. Electrolysis is conducted at a temperature of 55-65°C and a current density of 150 to 250 A/sq m. Current efficiency is 96 per cent at a voltage of 2.4-2.8 V in the case of sulphate electrolyte and 1.8-2.0 V in the case of sulphate-chloride electrolyte. For the extreme values of voltage, power consumption will be 1750 to 2920 kWh/ton of nickel. To avoid contamination, starting sheets which are 6 to 9 mm thick are often simply cut and shipped to the user without remelting.

Average anode nickel produces about 5 per cent of its weight of slime which settles to the bottom of the tank and contains copper, nickel, sulphur, carbon, slag inclusions and platinum-group metals. The slime is dried, calcined and melted into anodes for secondary electrolysis. The secondary slime is high in platinum-group metals and is sent for treatment to refineries.

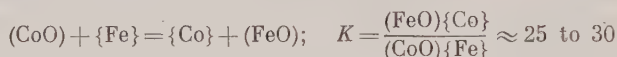
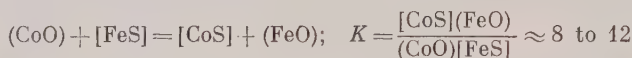
63. Cobalt Manufacture

Cobalt is a usual associate and a chemical analogue of nickel. In modern technology cobalt has found many uses, especially in the manufacture of diamond substitutes, heat-resistant alloys, acid-proof alloys, and magnetic alloys. A good proportion of cobalt comes from its recovery together with nickel from nickel ores or together with copper from copper ores.

In its affinity for oxygen and sulphur cobalt stands in between nickel and iron. Therefore, in the treatment of sulphide or oxide

nickel ores cobalt enters the nickel matte; when the matte is bessemerised to the complete removal of iron, the cobalt enters the converter slag. The concentration of cobalt in the latter may be 2 to 10 times greater than in the original ore.

To remove cobalt, the converter slag is remelted two or three times with nickel matte, pyrite, pyrrhotite or pig iron. As a result, the cobalt is withdrawn into a metallic or sulphide phase according to the reaction:*



Molten iron-cobalt alloy or cobalt-enriched matte is blown in a converter to slag off the iron and is then cast into anodes which are dissolved by an electrochemical method in either acids or a sodium chloride solution. In passing into solution, the cobalt is often accompanied by appreciable amounts of iron, copper, nickel and other impurities. A simplified diagram of the process is shown in Fig. 99.

The solution is freed of iron by oxidising the iron with chlorine and precipitating it as basic salts with additions of limestone or soda. The precipitate absorbs the impurities: arsenic, antimony and bismuth. The copper is cemented with cobalt or nickel powder; sometimes it is precipitated with soda. The manganese is removed by blowing the solution with chlorine or by adding sodium hypochlorite (NaOCl), which treatment produces a residue of $\text{MnO}_2 \cdot n\text{H}_2\text{O}$.

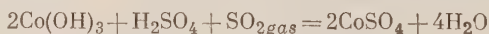
When the solution has been thus purified and only contains cobalt and nickel, the cobalt is precipitated by chlorine or sodium hypochlorite according to the reaction:



The concurrent precipitation of nickel is prevented by the exchange:



Should some nickel come down with cobalt hydroxide, which occurs when the ratio Ni/Co in the solution is high, the primary hydroxide is reprecipitated by the same method after dissolving it according to the reaction:



The final cobalt hydroxide is mixed with soda, calcined and washed with water to remove sulphur which is present as Na_2SO_4 .

* () gives concentration in slag, [] in matte, { } in the metallic phase.

After a repeated calcining, this time without soda, the resulting Co_3O_4 will carry 70-72 per cent Co, 0.2-0.3 per cent Ni, and a few hundredths of one per cent of other impurities.

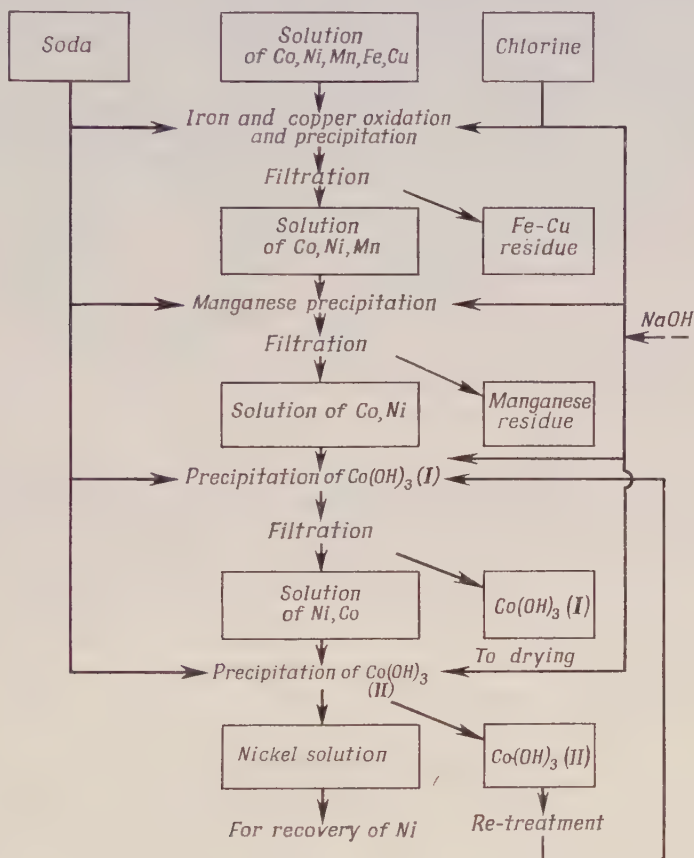


Fig. 99. Flow-sheet for cobalt recovery

Cobalt may be reduced from cobalt oxide in an electric furnace in the presence of a reducing agent low in sulphur, such as graphite. While molten, it is refined to slag off sulphur and to remove carbon. The metal is cast into moulds.

Cobalt of particularly high purity can be obtained by refining the cobalt matte electrolytically or by extracting it with organic solvents.

Apart from nickel ores, cobalt is smelted from copper-cobalt and cobalt-arsenic ores. These ores are concentrated by flotation and some other methods. Concentrates from copper-cobalt ores containing 0.5-10 per cent cobalt are either smelted or roasted and then leached with water. Cobalt-arsenic concentrates carrying 10-20 per cent cobalt are leached directly in autoclaves. In both cases, the cobalt-carrying solution is treated in a manner similar to the one illustrated in Fig. 99.

Chapter VIII

THE METALLURGY OF LEAD

64. General

Lead is a soft, malleable metal of dull, bluish-grey colour. It melts at 327.4°C and boils at 1740°C. Its density is 11.34 g/cm³ (for solid metal) and 10.69 g/cm³ (for molten metal near melting point). Being of relatively low melting point, lead readily vaporises beginning with about 1000°C, as can be seen from the pressure of its vapours:

Temperature, deg. C	700	1130	1290	1360
P, mm Hg	10 ⁻²	10	50	100

Lead has a face-centred cubic structure and no allotropic modifications. Its electrical and thermal conductivity and hardness are about one-tenth of copper's.

Lead is in Group IV, Period VI of the Periodic Table, and has two valencies, two and four, mostly forming double-charge cations. Lead and its compounds are very toxic. It can only dissolve in relatively concentrated acids while causing hydrogen to evolve. This is because its electrode potential is very low (−0.13 V) while hydrogen overvoltage on the metal is rather high (of the order of −1.0 V).

In some cases the dissolution of lead may be prevented by nearly insoluble salt films, such as PbSO₄, forming on its surface. At above 200°C lead readily dissolves in strong sulphuric acid:



Lead chloride is more soluble than lead sulphate. Lead is less stable against hydrochloric acid. In diluted nitric acid lead dissolves better than in concentrated, its nitrate being more soluble in water than in acid. Furthermore, HNO₃ causes oxidation of lead:



In concentrated solutions and melts of strong alkalis lead forms plumbites in which it is the basis of the anion PbO₃²⁻:



Many industries utilise the stability of lead towards sulphuric acid, diluted alkaline solutions, ammonia, chlorine, hydrofluoric acid, some organic acids, oils, etc.

In water lead is stable as it is covered by a protective coating of $\text{Pb}(\text{OH})_2 \cdot \text{PbCO}_3$. In the presence of much carbon dioxide, however, noticeable corrosion is likely to take place owing to the formation of the more soluble lead bicarbonate $\text{Pb}(\text{HCO}_3)_2$.

If melted in contact with air, lead is oxidised to litharge (PbO), the rate of oxidation increasing with heating. If the heating is continued, at a temperature of 330 to 450°C the PbO gradually changes to the sesquioxide (Pb_2O_3) which dissociates according to the reaction:



Only litharge maintains equilibrium with molten lead. In melts, litharge displays the properties of a base and may form silicates of the type $n\text{PbO} \cdot \text{SiO}_2$, ferrites of the type $m\text{PbO} \cdot \text{Fe}_2\text{O}_3$, arsenates of the type $x\text{PbO} \cdot \text{As}_2\text{O}_5$, antimonates of the type $y\text{PbO} \cdot \text{Sb}_2\text{O}_5$, etc.

Lead is one of the six so-called prehistoric metals. The ancient Egyptians used lead in glazing pottery. Later it was used in table wares, building, and, with the invention of fire-arms, in bullets and shot.

As more progress was made by the chemical industry, lead came to be used to protect chemical equipment. True, in our time this function is better performed by cheaper and less scarce plastics.

Advances in electrical engineering and communication also became possible owing to lead used as cable sheaths.

Another field of application was opened for lead when Planté invented his lead storage batteries. Today, a good deal of lead goes to make plates for storage batteries employed in motor vehicles, aircraft, wind-power plants, etc.

In recent years lead has attracted much interest in nuclear engineering. It has an extremely high density and is useful in protection from gamma rays (biological shielding).

Lead alloys readily with nearly all other metals in widely varying proportions. Its alloys of industrial importance include bearing or babbitt metals; solders; type metal; casting metals; and alloys used for the protection of electrical and chemical equipment.

Babbitt or bearing metals consist of lead, tin, copper, antimony, arsenic and cadmium and possess high antifriction properties and low melting point. A more recent trend has been to replace expensive tin with calcium and magnesium (lead-calcium and lead-magnesium babbitts).

Solders are commonly alloys of lead and tin, widely varying in the proportions of the two metals, melting point and uses.

Type metal originally consisted of lead and antimony. Now it often contains tin and copper. An ordinary type metal will have the following analysis: Pb, 72 per cent; Sb, 18 per cent; Sn, 9 per cent; and Cu, 1 per cent.

Alloys of lead, antimony and arsenic are harder and stronger than pure lead. An alloy containing up to 25 per cent Sb is known as antimonial or hard lead and is used to protect chemical apparatus. Lead alloyed with up to 3 per cent tin and up to 1 per cent antimony is used as sheathing for cables. Shot is made from lead alloyed with 0.2-1 per cent arsenic which increases surface tension and facilitates the casting of shot of regular shape.

Of the chemical compounds of lead, widest use is made of litharge (PbO) which goes into ceramics, glass, storage batteries and rubber.

Tetraethyl lead is used as an antiknock addition agent for petrol. Its formula is $\text{Pb}(\text{C}_2\text{H}_5)_4$.

65. Sources of Lead

Lead is produced from ores and industrial wastes. In ores lead occurs as a variety of minerals the most important of which are galena PbS , cerussite PbCO_3 and anglesite PbSO_4 . The greater proportion of all lead produced comes from galena-containing ores, however.

All lead ores contain substances other than lead minerals, the principal associates being zinc and silver. Sometimes, a lead ore will carry more zinc than lead. For this reason they are often termed lead-zinc ores and are treated for the recovery of both metals.

In sulphide ores zinc is often present as sphalerite or false galena and wurtzite (ZnS), or marmatite which is an isomorphic mixture of zinc and iron sulphides (Fe, ZnS). Silver in sulphide ores occurs as argentite Ag_2S and grey ore.

In oxide ores zinc is present as the mineral smithsonite ZnCO_3 and silver as metal or as AgCl .

Copper often accompanies zinc-lead ores in commercially attractive concentrations. In sulphide ores it occurs as sulphides, while in oxide ores it is present as malachite and azurite.

The other impurities occurring in complex lead-zinc ores are gold, bismuth, antimony, arsenic, cadmium, tin, gallium, thallium, indium, germanium, selenium, and tellurium.

The gangue of sulphide lead-zinc ores consists of pyrite, pyrrhotite, quartz, baryte, calcite and small amounts of the silicates of aluminium, iron, magnesium and calcium.

Ores may occur as continuous masses or as replacements in quartzites and siliceous shales.

An approximate composition of lead-zinc ores is given below:

Pb	Zn	Cu	Fe	S	SiO_2
0.12	1.35	0.6	5.0	5.0	—
2.3	2.5	1.0	1.8	—	20.0
1.6	4.0	0.5	8.5	16.0	19.0

The desire to recover all commercially valuable constituents from lead ores has stimulated the use of flotation in lead metallurgy. Not a single smelter produces lead directly from an ore now. Flotation has made valuable even low grades of ore containing as little as 0.3-0.5 per cent Pb.

Lead concentrates obtained by beneficiation of complex ores contain 40-78 per cent Pb, 4-7 per cent to 12-15 per cent Zn and 2-3 per cent Cu.

Where an ore carries more copper, it is possible to obtain a copper concentrate by flotation. In a few cases, pyrite concentrate can also be separated. Table 29 presents the flotation products of a complex ore.

Table 29
Flotation Products of Complex Ores

Product	% of total ore (by weight)	Content, per cent				
		Cu	Pb	Zn	Au, g/ton	Ag, g/ton
Original ore	100.00	3.14	1.08	6.96	0.72	37.0
Copper concentrate	9.41	27.8	2.3	4.86	3.67	163.0
Lead concentrate	1.44	3.7	47.2	14.5	6.6	73.4
Zinc concentrate	11.45	2.47	0.8	48.1	0.84	32.3
Pyrite concentrate	15.0	0.84	0.18	1.0	0.79	27.7
Tailings	62.7	0.1	0.1	0.98	0.01	0.05

Referring to the above table, the bulk of the precious metals is distributed between the copper and lead concentrates. Some of

Table 30

Distribution of Cadmium and Trace Elements between the Products
of the Differential Flotation of Lead-zinc Ores

Element	Distribution, per cent				
	Concentrates				Tailings
	lead	copper	zinc	pyrite	
Cadmium	2-12	—	39.9-74.1	—	5-56
Indium	2-6	—	2.3-66.0	—	4-93
Thallium	7.1-100	—	up to 5	up to 12	up to 90
Gallium	1.4-2	—	3.6-5.2	—	91-98
Germanium	up to 20	—	—	—	74-98
Selenium	24	19	—	20	30-87
Tellurium	32	10	—	13	30-87

the gold and silver is associated with pyrite which fact necessitates the separation of pyrite concentrate. Where no copper concentrate is separated, the precious metals usually go into the copper-lead concentrate, very little gold and silver passing into the zinc concentrate. Bismuth likewise shows preference for lead concentrates and cadmium for zinc concentrates, a factor serving as the basis for their recovery concurrently with lead and zinc.

Table 30 shows the distribution of cadmium and trace elements between the products of the differential flotation of lead-zinc ores.

Secondary lead is obtained from various wastes and scrap. At the present time, it accounts for 30-40 per cent of all lead produced.

66. The Art of Lead Ore Smelting

The chemical principles underlying the smelting of lead ores may be classed into three types: (1) the reduction of lead sulphide by metallic iron; (2) the reaction between lead sulphide and lead sulphate or oxide; and (3) the reduction of lead oxide by carbon or carbon monoxide.

The first principle is the basis of precipitation smelting. It produces lead and a sulphide matte which has to be treated additionally by some other method for the recovery of its lead. Though widely employed in the past for the treatment of high-lead ores, precipitation smelting has ceased to be used by itself on account of its complexity and high cost.

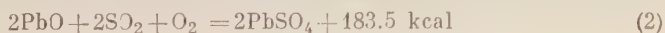
The second principle, known as air-reduction or roast-reaction, results in a double decomposition with the formation of lead and sulphur dioxide. This system of smelting is the basis of ore-hearth smelting used since ancient times and still employed by itself by some smelteries.

The third principle, involving the preparation of lead oxide, lead silicate or other oxidised compounds by roasting and sintering, has become the main system in the lead industry in the U.S.S.R. and other countries. Its flow-sheet is shown in Fig. 100.

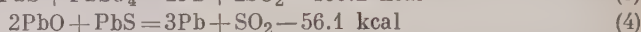
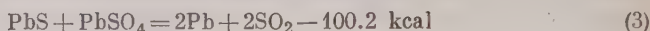
In practice, the principles are not so clearly delineated as theoretically stated, the reactions basic to one process invariably playing a definite part in the other process.

The types of furnaces which accomplish the last two principles are the ore-hearth and the blast furnace.

In ore-hearth smelting, the furnace resembles a blacksmith's hearth. The charge consists of almost pure galena and lime and is blown with air. The lead sulphide is oxidised thus:



The oxidation begins on the surface of the particles and reaches into the inside rather slowly. The interaction of the core with the oxide and sulphate on the surface produces metallic lead:



To make up for the loss of heat in ore-hearth smelting, a small amount of pulverised coal or coke is usually added to the charge.

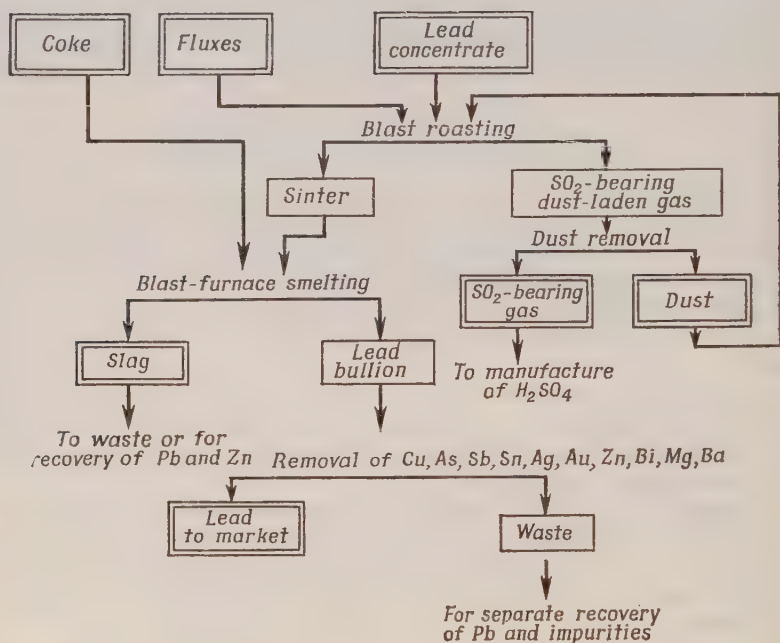


Fig. 100. Flow-sheet for roast-reduction lead smelting

The ore-hearth reactions proceed at 700-800°C which is not high enough for the charge to fuse, and it remains solid throughout the operation. As a result, the reduced lead trickles out sluggishly, and the reaction between the sulphides and oxides of lead is in the long run interrupted due to the fact that they are present in the charge in other than stoichiometric proportions. About 10 to 30 per cent of the lead goes into a 50-per cent product known as grey slag, which must be re-treated.

Fig. 101 shows an ore hearth. It is essentially a low cast-iron box surrounded by three cast-iron water jackets and fitted with a partial sheet-iron front wall. The cast-iron box measures about 2.5 m in length, 0.5 m in width, and 0.25 m in depth, the thickness of the

walls being 50 mm. The hearth box or lead basin rests on a brick-work or cast-iron stand. The partial wall or shutter leaves an opening 500 mm high the whole length of the front.

In the front there is an inclined cast-iron apron or work-plate with a groove to carry off the reduced lead into a kettle. The back

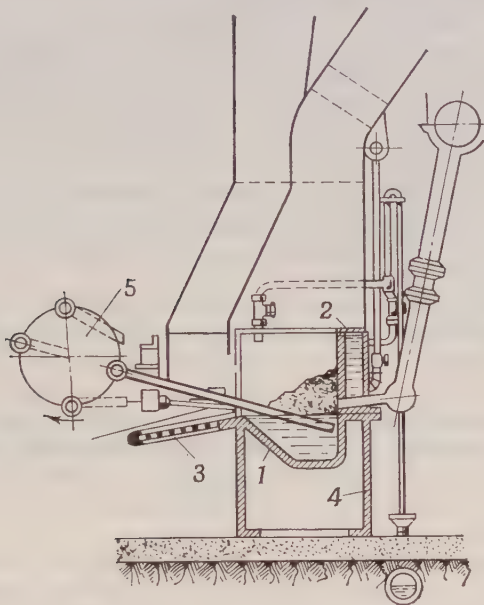


Fig. 101. Lead ore hearth:

1—lead basin; 2—water jacket; 3—work-plate (or apron); 4—stand; 5—rabbling mechanism

water jacket has tuyeres arranged in a single line somewhat above the edge of the hearth box.

The hearth is started by preheating the lead basin and filling it with molten lead. The charge made up of lead concentrate, lime, coke breeze or pulverised coal is introduced into the hearth so that it floats on the molten bath. The lime usually accounts for 2-3 per cent of the weight of the charge and is mixed with the concentrate before charging. The coal used amounts to 3-8 per cent of the weight of the charge. The fuel and the other constituents of the charge are introduced in alternate layers so that the materials form a slope from the rear wall towards the partial front wall, and the tuyeres are buried under the charge.

The air blown into the hearth through the tuyeres oxidises the lead sulphide; the products of oxidation react with the remaining lead

sulphide according to the reactions already discussed; and the metallic lead trickles through the charge to the bottom.

During the smelting operation the charge is stirred by a rabbling mechanism moving on overhead trackage along the front of the hearth. The end of the rabble arm dipped into the molten bath moves both vertically and forward.

The hearth attendant withdraws some of the charge onto the inclined work-plate at regular intervals. The reduced lead trickles down the groove and into an outside kettle; grey slag is removed; and the material that has not yet reacted is returned to the hearth.

The waste gases are withdrawn through a flue and into a dust catcher. Up to 25-30 per cent of the charge by weight passes off in the waste gases, for which reason careful dust treatment is very essential in ore-hearth smelting. The coarser dust settles in the flue and settling chamber, while the finer dust is caught in bag filters and electrostatic precipitators.

When working concentrates containing 70-75 per cent lead, the direct recovery usually is 70 per cent; full recovery, including the lead recuperated from the grey slag and dust, is 95-97 per cent.

In ore-hearth smelting, 65-70 per cent of the metal makes up lead bullion, 15 per cent grey slag, and 15-20 per cent dust. These figures are convincing enough to show that under modern conditions ore-hearth smelting may only be employed as an auxiliary process by which a proportion of lead may be recovered from rich concentrates with little fuel and flux used.

The output of ore-hearths is 6 to 10 tons of concentrate per 24 hours per linear metre of lead basin length. Lead basins longer than 2.5 m are not built because of inconvenience in servicing.

The chemical principle similar to ore-hearth smelting is employed by one smelter in electric furnaces. The source material is a sulphide concentrate containing 65-70 per cent lead. Prior to smelting, it is nodulised with recycled sinter and flue dust and sintered on sintering machines at 800°C.

About 96 per cent of the metal is withdrawn as bullion, leaving 3-4 per cent in the slag. With very little flux used, the amount of slag produced is insignificant. Power consumption is 450 kWh/ton of charge.

Among the advantages offered by this process are high output (reaching 5 tons per square metre per 24 hours), the possibility of using high-grade charge containing 65-70 per cent lead, and healthier working conditions than in blast-furnace or ore-hearth smelting.

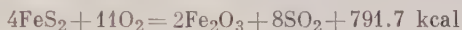
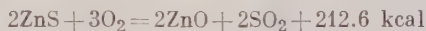
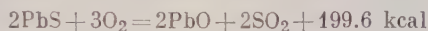
Another smelter is using the air-reduction principle in short-drum furnaces, also maintaining high daily output and healthy working conditions.

67. Blast Roasting of Lead Concentrates

When a concentrate is roasted on a sintering machine (so-called blast roasting), the sulphides are self-burned and sintered under air blast as the air is drawn through the bed of material by suction. The good contact between the air and the sulphides and the high temperature of the operation raise the rate of oxidation much above what is attainable in multiple-hearth roasters.

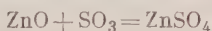
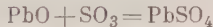
The sulphides are ignited at the surface of the bed by the flame of the ignition hood. As the ignition hood moves above the suction chambers, the lower layers ignite consecutively.

Blast roasting involves the following reactions:



Most of the heat generated during roasting comes from the combustion of PbS, for other sulphides are present in the concentrate in small amounts. The sulphides of antimony, arsenic, copper and silver are oxidised to form oxides.

The sulphur dioxide is partly oxidised to sulphur trioxide. The latter forms sulphates with the metal oxides:



Sulphates of copper and silver may likewise be formed.

The sulphates of lead and zinc are most stable and will only decompose at over 1000°C. The arsenic trioxide partly passes off in the waste gases, and partly is oxidised to slightly volatile pentoxide. The antimony is oxidised by roasting to tri-, tetra- and pentoxides, the lowest oxide being markedly volatile.

The acid oxides of the metals in the bed of the charge react with the basic oxides to form silicates, ferrites, arsenates and antimonates of lead, iron, zinc, etc.

The oxides of lead and cadmium, the sulphides of lead, antimony and tin, as well as metallic lead have, at the roasting temperature, appreciable vapour pressures (Table 31), and partly pass off in the waste gases.

The sintering effect is attained owing to the formation of low-melting compounds and alloys. The lead silicates and their alloys with lead oxide melt anywhere between 670 and 883°C. The eutectics in the system $\text{SiO}_2\text{-FeO-CaO}$ melt at 1030-1050°C. The sulphides and their alloys melt between 800 and 1400°C.

Premature sintering is undesirable, because the low-melting material may envelope unoxidised sulphide particles, shutting off

Table 31

Volatility of Some Metals and Their Compounds
(Approximate data)

Metals or compounds	Vapour pressure, mm Hg, at deg. C	
	750-850	1000-1100
Lead	2.6×10^{-2}	5-6
Lead oxide	0.1	4-15
Lead sulphide	2	17
Antimony sulphide	9	130
Arsenic trioxide	over 760	—

air, and the sinter will contain unburned sulphur. On the other hand, it is essential that the roasting be completed at 1000-1100°C, if the sulphates are to be completely decomposed and the sinter to be of good quality.

Both requirements are satisfied by adding ground smelting flux and revert fines to the materials to be sintered. These additions open up the texture of the charge and separate the concentrate particles from one another. Besides, the limestone added as flux decomposes during the roasting into CaO and CO₂; its decomposition is endothermic and prevents the temperature from rising rapidly. A similar effect is attained by adding as much as 8-10 per cent water to the charge prior to ignition. Fine, dry concentrate may pack so dense that the passage of air through the charge would be impossible. The water added to the material to be sintered makes it porous and reduces dust formation in charging.

A more recent method for the preparation of fine ores for smelting is known as pelletising. The powdered charge with an addition of moisture is added into a rotating drum or an inclined pan. As the drum or pan rotates, the material forms pellets up to 20 mm in diameter which are then conveniently sintered on a sintering machine. Fig. 102 shows a pan pelletiser 4.2 m in diameter with a capacity of up to 50 tons/hr or more.

Usually, 10 to 20 per cent sulphur is present in the charge, while in the sinter it should not run more than 2 per cent. This calls for a desulphurisation of 80-85 per cent—a level unattainable by a single-pass operation, because an ordinary sintering machine can eliminate 70 per cent of the sulphur at the most. As a way out, the charge to be sintered is made up of some green concentrate and sintered fines returned after screening to the sintering plant. The

returns are kept down to two or three parts to one part of the green material, thereby reducing the sulphur content of the charge to 5-6 per cent and making a single-pass operation possible.

Better results are obtained with what is known as double-over sintering in which the charge is passed through a sintering plant twice. The first sinter is obtained at 850-900°C and carries 6-7 per

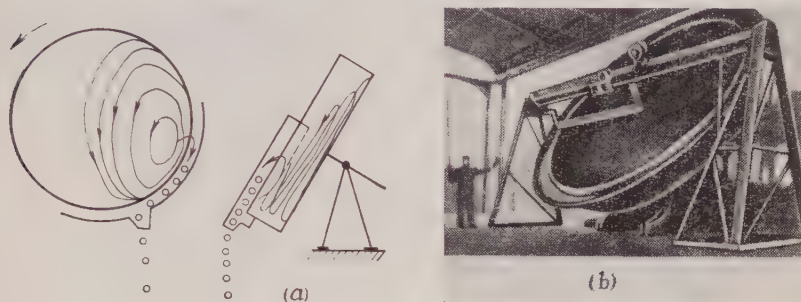


Fig. 102. Pan pelletiser:
(a) action of the pelletiser; (b) general view

cent sulphur; it is ground and resintered at 1000-1100°C; the sulphides are completely oxidised, the sulphates decomposed, and a strong sinter produced.

Single-pass sintering produces a sinter which runs less sulphur than in the case of the double-over process, as the returns actually go through the machine more than once. The advantages of this system, however, are to some extent offset by the necessity to grind, handle and mix a considerable quantity of hot and dusty returns. In present-day practice, use is made of both processes, the former being resorted to more often where a high-zinc charge is involved and more sulphur has to be eliminated.

The flux added to the charge to be sintered is usually broken down to 6 mm in jaw or rotary cone crushers, while the returns are ground in rolls to 8 mm. Further reduction in size, although it would make the charge with minus 0.1 mm green concentrate more uniform, does not pay, because the charge becomes less permeable to wind-box gases.

The sinter feed, after mixing, is transferred by an apron feeder into a moistener whence it is charged onto the pallets by a swinging spout which oscillates at right angles to the long axis of the machine (Fig. 103).

The swinging spout forms a bed of material over the entire width of the pallets. As the pallets move on, a stationary cutter shaves

off the bed to obtain any desired depth. The depth of the bed is usually set at 80 to 300 mm, depending on the gas permeability of the material.

The extent to which the sulphides are oxidised depends on the time of the pallet over the wind-box. The rate of pallet travel ranges between 0.6 and 1.5 m/min. The rate of sulphide combustion

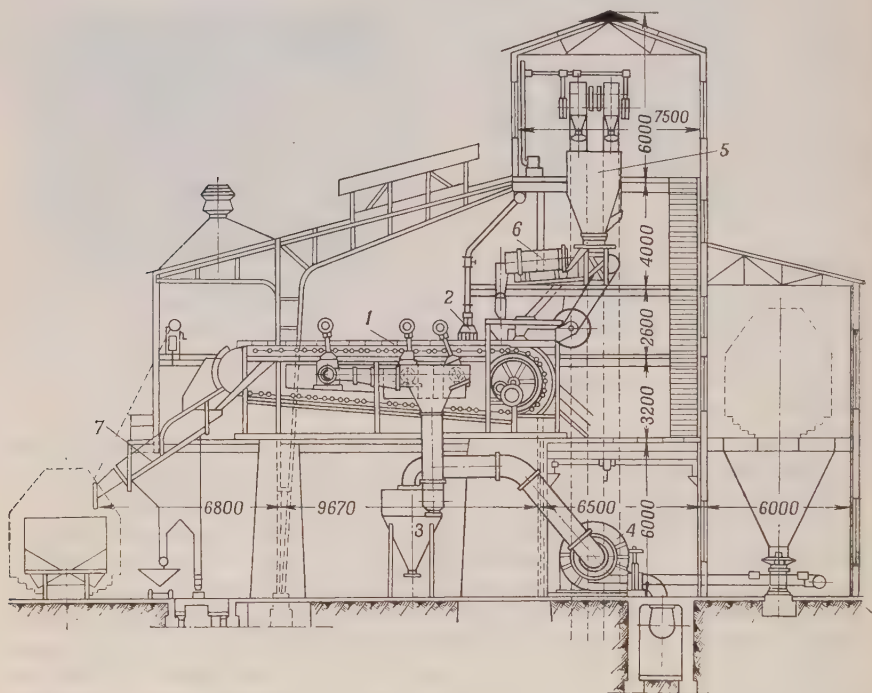


Fig. 103. Sintering plant:

1—pallets; 2—ignition hood; 3—cyclone; 4—wind-box; 5—charging hopper; 6—moistener; 7—screen

and the temperature in the bed are both dependent on the quantity of air drawn through the bed and can be controlled by varying the suction in the wind-box.

The exhaust gases of the sintering process contain sulphur dioxide, fumes of volatile matter and dust. The dust is caught in baghouses, the purified gases may be used for conversion to sulphuric acid if their sulphur dioxide content is over 4 per cent. The highest concentration of sulphur dioxide is obtained from the charge-end wind-boxes. As more sulphur is burned in the charge, SO_2 concentration decreases. To prevent the dilution of the charge-end gases with

those from the discharge end, the wind-box is divided into several compartments, and the exhaust gases from the last half of the machine are recirculated to the hood covering the first half of the bed to be again drawn through the feed. By this means, the final exhaust gases have a much higher SO_2 concentration.

The daily output of a sintering machine using the double-over process is 25-30 tons per square metre of pallet area in the first stage and 13-36 tons per square metre in the second stage. The fines not suitable for blast-furnace smelting may account for 10-15 per cent and are returned to the sinter feed.

A more recent trend has been to use an upward blast instead of downward suction in sintering, the suction chamber being converted to a wind-box building up a pressure instead of a suction. The air passing upwards reduces the wear of the pallets and provides for an easier recirculation of the exhaust gases.

The dust from the exhaust gases may be removed either in electrostatic precipitators or in baghouses. Baghouses use cotton or woolen bags 160-220 mm in diameter and 2.8-3.5 m long, and depend for their operation on the suction-induced passage of dust-laden gases through the fabric.

Fig. 104 shows diagrammatically a typical baghouse unit. The dust-laden gas is delivered by a pipe 9 under a horizontal partition with outlets to which the open end of bags 1 are attached tightly. By their closed ends the bags are suspended from a frame coupled to a mechanical shaker 6. The gas is drawn through the bags by an exhaust fan 2 to be discharged through a pipe 3. The dust settles on the inside of the bags. At regular intervals the shaker shakes the frame supporting the top ends of the bags. While the bags are being shaken, a damper 10 automatically shuts off the inflow of gas. The dust falls from the bags into hoppers 12 and is withdrawn by a helical conveyer 8.

Baghouses remove up to 99 per cent dust and are cheap to service and maintain. Their throughput, however, is very low, being 1-2.5 cum of gas per square metre of filtering area per minute. Large lead smelters would require too big and cumbersome baghouses, for which reason they have mainly been used at small smelting units where dust loads are relatively small.

The temperature of the incoming gases in baghouses should not exceed 100 C, or the bags will burn. On the other hand, it is important that the interior of the system be maintained above the dew point, or the dust may cake on the bags, thus reducing their efficiency.

In baghouses operated at higher throughputs, it is customary not only to shake the bags at frequent intervals but also to blow them with air in the direction opposite to the flow of the gas. These

baghouses are divided into sections some of which are disconnected from the system when desired and blown with air to remove the dust settling on the fabric.

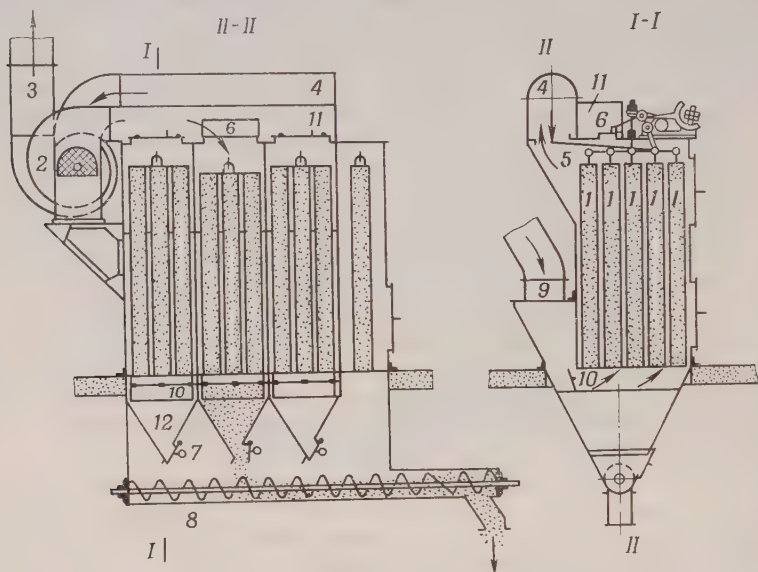


Fig. 104. Baghouse:

1—bags; 2—exhaust fan; 3—exhaust pipe; 4, 5, 11—gas off-takes; 6—shaker; 7—hopper gate; 8—helical conveyor; 9—dust-laden gas inlet pipe; 10—damper; 12—dust hoppers

Electrostatic precipitators have greater throughputs but are less efficient in catching the dust which consists mainly of lead and zinc oxides.

68. Blast-furnace Smelting of Lead Bullion

After blast roasting the material is smelted into lead bullion in blast furnaces similar in construction to those employed for copper and nickel smelting.

The crucible, or hearth, of a lead blast furnace is built into a rectangular iron shell carried by a concrete foundation. The walls of the crucible are built up of firebrick lined on the inside with magnesite brick. The crucible bottom has the shape of an inverted arch to prevent the bottom bricks from floating when the crucible is filled with molten lead. The shell is braced by I-beam lintel girders. The crucible usually is 600-700 mm deep.

Molten lead may be continuously tapped from the crucible through a siphon tap (Fig. 105), an opening measuring 25 cm square

in the crucible wall. It consists of a channel leading from the bottom of the crucible wall inside to a disk-shaped basin, the lead well, outside. When the crucible is filled with molten metal, excess lead overflows down the siphon tap and into the well from which it is transferred into a kettle. The use of a siphon tap is possible owing to the low melting point of lead. Should the siphon tap be closed, molten lead may be tapped from holes made level with the crucible bottom. Usually, the siphon tap is placed in one of the side walls of the rectangular section.

The water jackets of a lead blast furnace are similar to those of a copper smelting furnace, except that they are lower and are

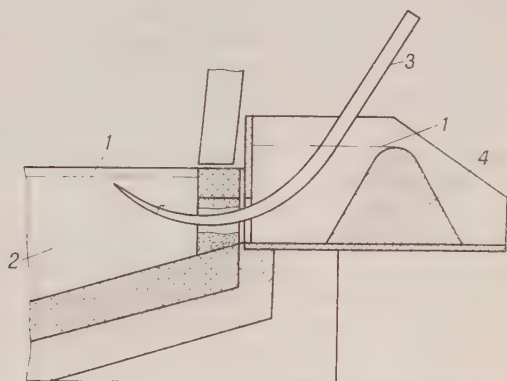


Fig. 105. Siphon tap of a lead blast furnace:
1—lead line; 2—hearth;
3—rabble; 4—clay dyke

arranged in two tiers, one above the other. The lower tier of water jackets carried by the crucible has an outward bosh of $5-7^\circ$, while the end water jackets are straight. Some of the water jackets known as tap jackets are metal slabs with embedded water coils and openings for slag tapping.

The tuyeres and the jacket cooling system are similar to their counterparts in copper blast furnaces. Until quite recently, the tuyeres were usually arranged in a single row, with two tuyeres per water jacket. A more recent trend has been towards a different arrangement in which the tuyeres are staggered in two rows spaced on 200-300 mm centres, so that there are three or four tuyeres per water jacket. This arrangement has appreciably improved the running of the blast furnace. The usual diameter of tuyeres is 100-125 mm.

The charging and gas-withdrawal facilities are similar to those used in copper and nickel smelting furnaces. A recent innovation has been the use of a double bell-and-hopper and a hermetically sealed top—two features which have appreciably improved the working conditions in the shop.

Lead blast furnaces are usually 10 m long, up to 1.6 m wide on the line of the tuyeres, and the distance from the tuyeres to the feed floor is 4-6 m (Fig. 106).

The smaller size of a lead blast furnace in comparison with a copper blast furnace is owing to the fact that the charge carries more metal, the respective figures being 35-50 per cent Pb and 1-2 per cent Cu.

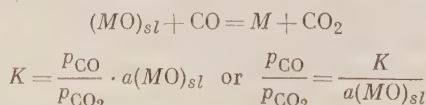
The temperature in the tuyere zone of a lead blast furnace usually is 1250-1300°C, reaching 1550°C in some places. The products of combustion rise up the shaft through the descending ore column, giving up their heat to the charge. The temperature in the crucible is lower than in the tuyere zone, being 900-1200°C. The flue gases leave the furnace at 250-400°C.

The composition of the blast-furnace gases varies as they ascend the shaft. In the tuyere zone the carbon of the coke burns to CO₂. The carbon dioxide, as it rises up, comes in contact with the red-hot coke and is converted to carbon monoxide. Further up the shaft, the CO content is reduced and that of CO₂ increases mainly due to the reduction of metal oxides.

During blast roasting, the bulk of the lead is combined into silicates which melt at 650-700°C. Soon after the charge has been introduced into the furnace, the silicates begin to melt and dissolve the oxides of other metals. Therefore, in blast-furnace smelting, the oxides of lead, iron and other metals are mainly reduced from the molten silicates trickling down against the ascending column of hot reducing gases.

The gases move through the charge at a relatively high velocity, and there is no time for an equilibrium between the solid carbon and CO₂ to be attained. The practical relationships between gas composition and temperature are shown in Fig. 107 by a cross-hatched area whose width indicates possible limits in one and the same horizontal section of the shaft. Referring to Fig. 107, when the temperature is high, the lower levels of the charge will contain more CO₂ than would be expected on the basis of the equilibrium curve. The same is true of the CO content in the upper levels of the charge when the temperature is low.

In a general form the reduction of oxides from the silicate melt may be presented as follows:



For an oxide to be reduced from slag, the concentration of CO in the gases must be the higher, the lower is the oxide content in the slag. As more oxide is reduced from the slag, the equilibrium curve

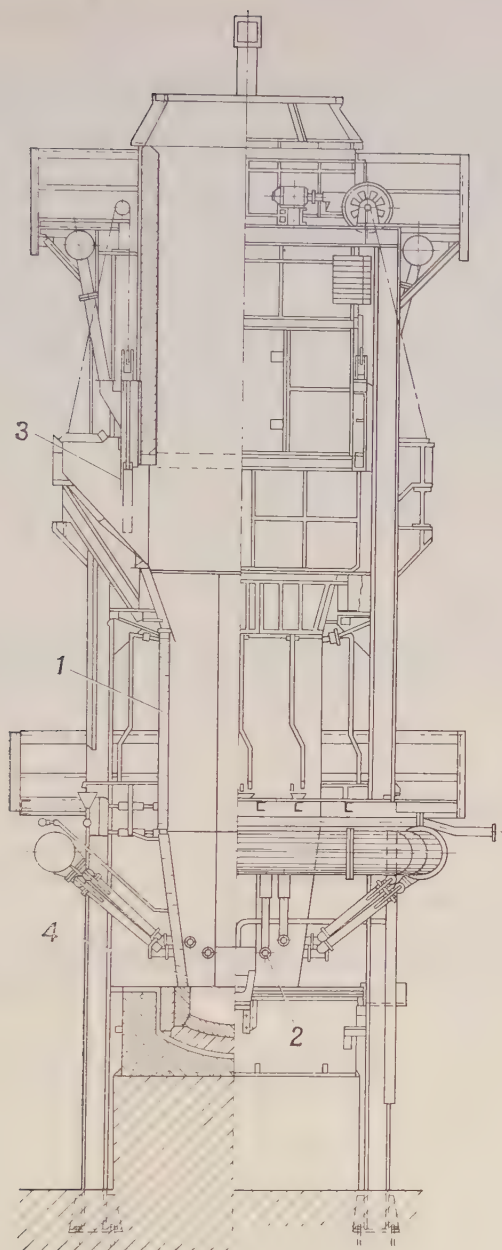


Fig. 106. Lead blast furnace:
 1—water jacket; 2—tuyeres; 3—charging doors; 4—siphon tap

for lead will move away from the equilibrium curve for a free oxide, rising above it as shown in Fig. 107.

The equilibrium curve for the reduction of free FeO to metallic form is located in the diagram fully within the area of reducing gases. Yet, in lead smelting practically no iron is reduced to metal because the equilibrium curve for the FeO dissolved in slag lies considerably higher than that of free FeO. Sometimes, however,

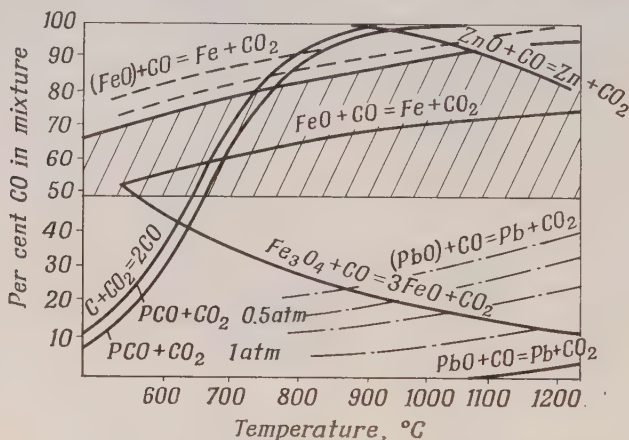


Fig. 107. Diagram showing the reduction of metals in roast-reduction smelting of lead ores:

- — — equilibrium curves for FeO shift as more iron is reduced from the slag;
- - - - - equilibrium curves for PbO shift as more lead is reduced from the slag

particles of metallic iron are found in the slag. The incidental reduction of iron to metallic form grows less probable with decreasing content of iron oxides in the charge and slag.

By applying the above reasoning to the reduction of lead and iron when the gas composition remains unchanged at some point in the furnace, we obtain:

$$\frac{p_{\text{CO}}}{p_{\text{CO}_2}} = \frac{K_{\text{Fe}}}{a_{(\text{FeO})_{sl}}} = \frac{K_{\text{Pb}}}{a_{(\text{PbO})_{sl}}}$$

or

$$\frac{a_{(\text{FeO})_{sl}}}{a_{(\text{PbO})_{sl}}} = \frac{K_{\text{Fe}}}{K_{\text{Pb}}}$$

The equilibrium constant K gives a measure of the change in the standard free energy for oxide reduction, or the affinity of a metal for oxygen, as $\Delta G = -RT \ln K$.

Iron has a stronger affinity for oxygen than has lead. Therefore, it is possible to maintain the temperature in the shaft and the con-

centration of CO in the furnace gases so that practically all lead will be reduced while the iron will be slagged as FeO.

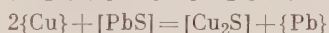
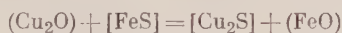
Blast-furnace slags usually assay 0.6-1.5 per cent PbO and 35-55 per cent FeO.

Furthermore, partial reduction of iron does not contaminate the lead, as iron is practically insoluble in molten lead. Nevertheless, every attempt is made to prevent the iron from being reduced, as it forms wall accretions which handicap the running of the furnace. On top of it, a slag low in FeO is of a poorer quality.

Alongside with the lead, the copper, bismuth, antimony, arsenic, zinc and other metals present in the charge are reduced and dissolve in the molten lead. Their solution facilitates their reduction on account that the free energy of solution is added to the free energy of reduction. Like the lead, the bulk of the impurity metals is reduced from the molten silicates.

Experience shows that sulphates are reduced quicker than they are decomposed. So, in lead smelting, desulphurisation does not usually exceed 20-40 per cent.

The sulphides of lead, copper and iron form matte which melts at anywhere between 950°C and 1100°C. Irrespective of the metal with which the sulphur of the sinter has been combined, the matte will consist of the metals having the greatest difference in their affinity for sulphur and oxygen, i.e., copper, lead and iron. The final composition of the matte depends on its reaction with the slag and bullion lead:



As the smelting operation progresses, the composition of the matte changes, approaching an equilibrium between slag and metal.

The matte of lead smelting has a specific gravity of 4.8-5.2, and so in the crucible it floats above the molten lead but below the slag.

Silver and gold are present in the sinter in elemental form (silver is also present as Ag_2S). Molten lead and matte dissolve them well, and so almost all of the gold and silver present is collected by the lead and matte. The recovery of the precious metals from the matte involves additional metal losses and capital outlays. Therefore, lead smelting without matte is a more attractive proposition.

On the other hand, matte smelting has to be employed when using concentrates high in copper.

The quantity of matte produced depends on the sulphur content of the sinter. In the case of a dead-roasted concentrate the copper

will be completely reduced to metallic form and will dissolve in the lead. In the crucible where the temperature is lower than in the tuyere zone, the copper may crystallise out, clogging the siphon tap and forming accretions on the walls, thereby reducing the capacity of the crucible. The copper crystallising in the siphon trap upsets its normal operation. This is the reason why in the blast roasting of lead concentrates high in copper, as much sulphur is left in the sinter as may be necessary for matte formation. Then the bulk of the copper will pass into matte, and no copper crystals will be formed either in the crucible or the siphon tap.

Concentrates carrying much copper and zinc are usually given a dead roast.

Zinc sulphide is more dangerous than copper: forming a zinc mush, it makes the slag sticky and handicaps the settling of molten lead. On the other hand, zinc oxide dissolves well in slags, especially in those running much iron, without impairing their fluidity. The formation of coppery accretions can be controlled by raising the temperature of the crucible.

Lead reduction smelting differs little from other blast-furnace processes. As has been noted elsewhere, fluxes are introduced into the charge prior to roasting. Sometimes, some, especially gold-bearing, flux is added directly to the charge in the furnace, thereby avoiding expensive grinding.

The bulk of the charge consists of lumps measuring up to 100 mm across. The fines less than 25 mm across should not exceed 10-15 per cent. The charging rate is maintained so that the quantity of material on the feed floor remains constant.

The height of the ore column has a direct bearing on the progress of the smelting operation. In the case of a high ore column, which is 4.5 to 6 m, the temperature of the flue gases should not exceed 150 to 250°C. A high ore column traps fines well, and so little dust is carried off with the gases.

Operation with a low charge column, which is 2.4 to 2.7 m high, has its merits and demerits. On the one hand, the higher velocity of the gases through the charge, the expanded zone of coke combustion and the higher temperature of the top gases (500 to 1000°C) speed up the running of the furnace, increase its daily output, and eliminate more sulphur. On the other hand, a considerable proportion of metals and their compounds is volatilised, much dust passes off with the flue gases, and much lead is lost with the slag due to incomplete lead reduction. As a result, the slag has to be re-treated, additional dust-catching equipment installed, and a greater dust load handled. For these reasons, lead smelting practice uses a high charge column more often than a low one.

The stream of slag and matte tapped from the furnace breast flows into a forehearth where they are separated. The separate tapping of the matte is unfeasible because it forms a very thin layer in the crucible. The forehearths of lead blast furnaces are usually made mobile, mounted on trucks, and are built up of cast-iron plate.

To be good for lead smelting, slags should melt at 1150-1200°C. Too low melting slags would melt and trickle down into the crucible before the lead oxide in them has had time to be reduced; too high melting slags would involve increased fuel consumption.

The principal role of slags is to withdraw the iron oxides and silica—the predominant impurities in the sinter. Slags consisting solely of FeO and SiO₂ are heavy and separate from the matte with difficulty. In addition, the relatively low melting mixtures of these oxides are high in FeO, and so the iron may be reduced to metallic form during smelting.

Calcium oxide added as a third component reduces the specific gravity of the slag and enhances the reduction of lead by increasing the activity of the PbO in the slag.

The approximate composition of several lead-smelting slags (in per cent) is tabulated below:

SiO ₂	FeO + MnO	CaO	ZnO	Al ₂ O ₃	Cu	Pb
29.9	37.1	18.5	3.0	9.7	0.1	1.5
35.0	34.3	18.5	6.0	3.6	—	0.9
25.0	37.0	15.0	12.0	8.0	0.16	1.6
24.8	39.8	9.7	18.0	6.9	0.9	2.3
10.7	16.8	4.0	29.1	3.0	0.85	2.9
13.5	41.0	4.7	38.5	—	—	3.0

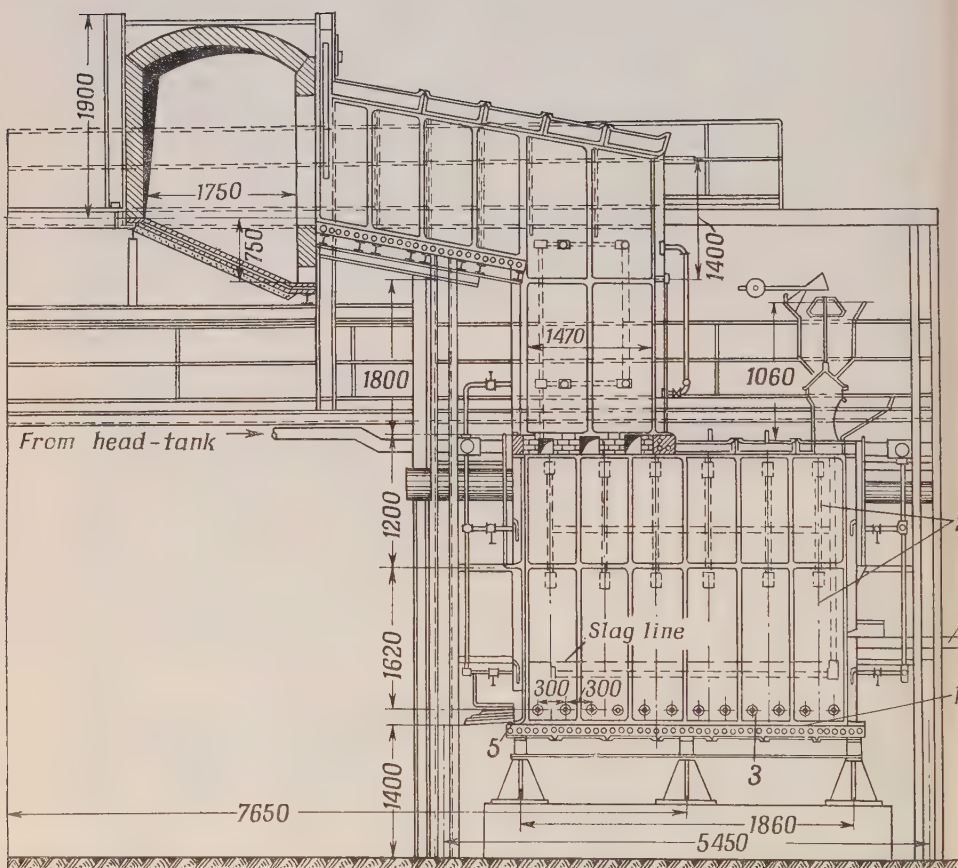
Zincy lead charge requires that the slag be capable of dissolving large quantities of zinc oxides. The solubility of zinc oxide increases with increasing FeO and decreases with increasing SiO₂ and CaO in the slag.

According to Loskutov, a good lead-smelting slag should have a viscosity of not higher than 5 poises at 200 C, if heavy losses of lead are to be avoided. With a less fluid slag, more lead is lost due to incomplete separation of the matte and lead—while the non-reduced lead oxide runs not more than 0.2-0.4 per cent, the lead carried by the slag amounts to 1.5-2 per cent.

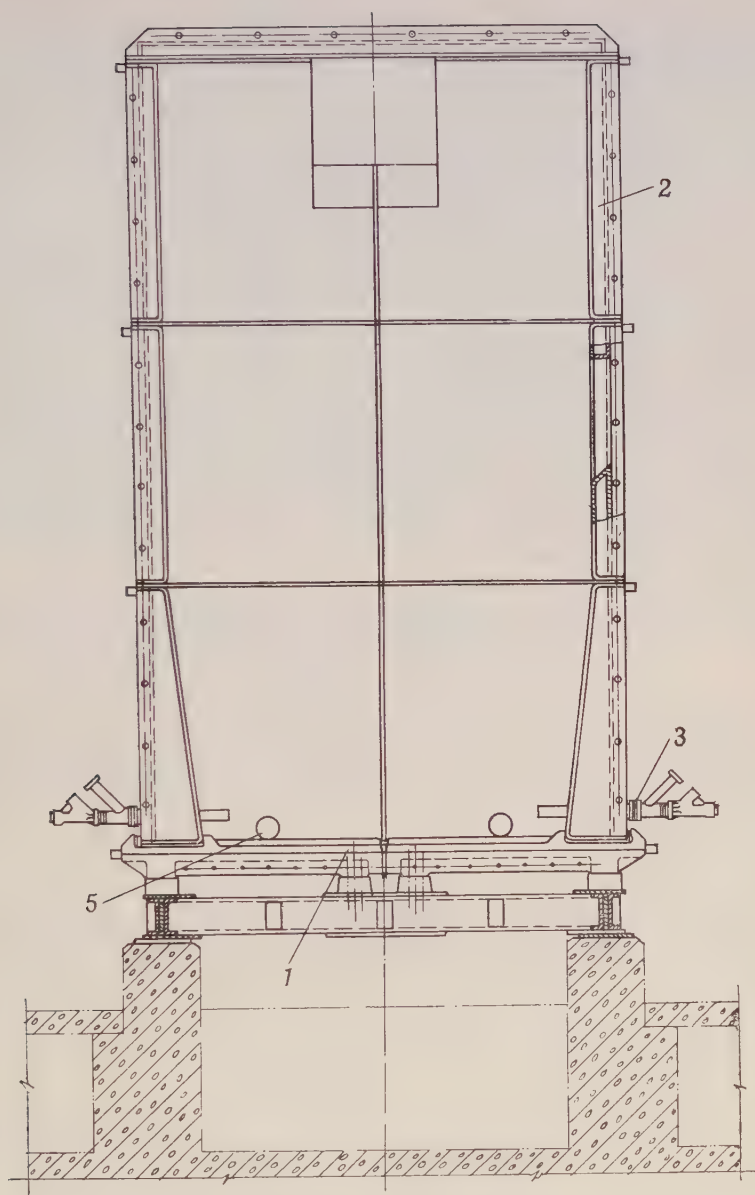
The losses of the precious metals with the slag increase in proportion to their content in the charge and to lead losses. Most of the gold and silver is lost with the drops of matte and lead caught in the slag. Lead-smelting slags usually assay up to 15 grams of silver per ton.

Fig. 108. Slag-fuming furnace: ►

(a) longitudinal section; (b) transverse section;
 1—hearth; 2—water jackets; 3—tuyeres; 4—slag pouring chute;
 5—tap holes



(a)



(b)

The approximate compositions (in per cent) of several copper-lead mattes are given below:

Pb	Cu	Fe	S	Zn
11.16	1.6	41.3	22.2	11.6
18.0	4.8	57.0	16.8	6.5
14.8	9.5	37.5	20.5	—
9.1	15.0	37.9	22.0	5.4

The top gases immediately above the charge column carry much carbon monoxide. It is heavily diluted with air and therefore unsuitable as a fuel. With a better sealed furnace top, it would be possible to utilise the carbon monoxide.

The dust carried off with the flue gases partly settles in the flues while the fines are caught in electrostatic precipitators or in baghouses. The dust from the flues is returned into the roasting charge; the fines which collect the cadmium and rare metals issuing from the furnace as fumes are re-treated to recover their valuable burden.

The composition of the dust caught from lead-smelting gases by electrostatic precipitators and baghouses is given below:

Cd	Pb	Zn	As
0.40	77.8	2.51	0.045
1.57	63.83	13.20	0.34
2.30	57.58	8.80	0.54

The daily output of modern lead blast furnaces ranges between 45 and 60 tons per square metre of crucible area. As to other furnace characteristics, they are to a considerable extent dependent on the composition of the charge and are greatly improved by enriching the blast with oxygen.

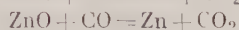
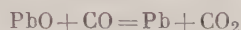
The extraction of lead into bullion depends on the quantity of matte and slag produced and their lead content. Very little matte and slag is produced when smelting rich copper-free concentrates, and the lead recovery may be as high as 95 per cent. When smelting copper-bearing concentrates, the matte produced accounts for 8 to 10 per cent of the charge by weight. When the charge carries much both zinc and copper the recovery of lead is reduced to 90 per cent.

Some lead smelters recover drops of lead and matte entrapped by the molten slag by allowing the latter to settle in large stationary forehearths heated with fuel oil, pulverised coal, gas or electricity. This type of forehearth is in fact a small reverberatory or electric furnace where the slag flows continuously from the blast furnace.

The lead and zinc oxides dissolved in the slag may be withdrawn by any of the fuming processes, using a slag-fuming furnace.

A slag-fuming furnace consists of water jackets set up on a water-cooled cast-iron baseplate (Fig. 108). The furnace measures from 2.5 m by 3.5 m to 3 m by 7 m in plan and from 3 to 10 m in

height. The sides have from 11 to 36 tuyeres up to 100 mm in diameter. Molten slag is poured into the furnace to a level above the tuyeres, and pulverised coal is blown through them and into the charge, the coal serving as both a reducing agent and fuel. Inside the air bubbles floating to the surface the coal burns to CO which reduces the oxides of lead and zinc from the slag. The coal particles floating in the slag also contribute to the reduction reaction but mainly due to the gas envelopes forming around them:



The temperature in the furnace being about 1300°C, the reduced metals and lead sulphide vaporise, their vapours are carried to the surface of the slag to be oxidised and carried off by the gases as a fine dust containing 15-25 per cent lead oxide and 60-75 per cent zinc oxide. The heat of the gases is utilised by waste-heat boilers, and the fine dust is then recovered from the cooled gases in baghouses. The coal-fired slag-fuming process is capable of recovering up to 90 per cent zinc and 95-98 per cent lead from the slag. The dust thus obtained is disposed to zinc plants. Coal-fired slag-fuming furnaces operate intermittently, every cycle lasting for 2 hours and treating 40-50 tons of slag. Coal consumption is about 20 per cent of the slag weight.

69. Refining of Lead Bullion

General. The composition of lead bullion (in per cent) lies in the following range: Pb, 92-99; Au, 0.0001-0.05; Ag, 0.05-0.8; Cu, 0.1-7.0; Zn, 0.006-1.3; As, up to 1.9; Sb, 0.1-1.5; Bi, up to 0.3; and Fe, up to 0.25. The composition of the commercial grades of lead is presented in Table 32.

Table 32

Composition of Commercial Lead Grades
(per cent)

Grade	Pb, min.	Max. impurities										
		Ag	Cu	As	Sb	Sn	Zn	Fe	Bi	Mg	Ca+ +Na	total im- pu- rities
CB	99.994	.0003	.0005	.0005	.0005	.001	.001	.001	.004	.001	.002	.006
CO	99.99	.0005	.001	.001	.001	.001	.001	.001	.005	—	.003	.01
C1	99.98	.001	.001	.002	.004	.002	.001	.002	.006	—	.003	.02
C2	99.95	.0015	.001	.002	.005	.002	.002	.003	.03	.005	.02	.05
C3	99.9	.002	.002	.005	—	.01	.005	.005	.06	.01	.04	.10
C4	99.5	.002	.09	—	.25	—	.10	.01	.10	.02	.10	.50

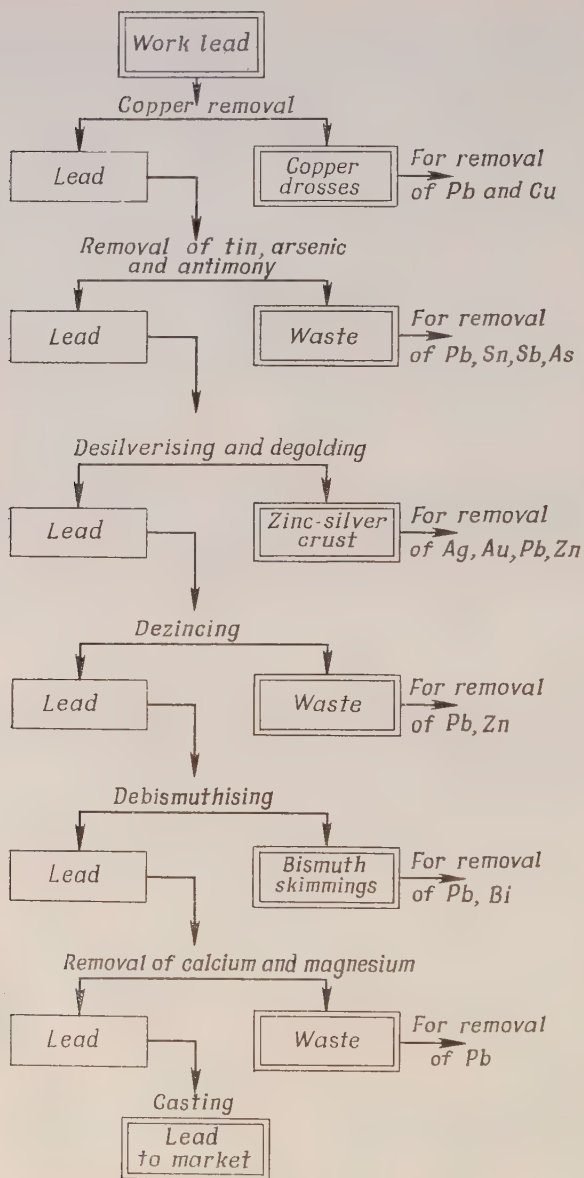


Fig. 109. Flow-sheet for pyrometallurgical refining of lead bullion

The difference in composition between lead bullion and commercial lead grades forcefully proves the necessity of lead refining.

The task of lead refining is not only the concentration of a bullion, but also the removal of the impurities in a form suitable for their subsequent working to pure metals, especially the precious metals whose content may be worth more than the lead itself. Lead bullion can be refined pyrometallurgically or electrolytically.

Pyrometallurgical Refining. A flow-sheet for the pyrometallurgical refining of lead bullion is shown in Fig. 109. The key piece of refining plant is a cast-iron or steel kettle heated with fuel oil,

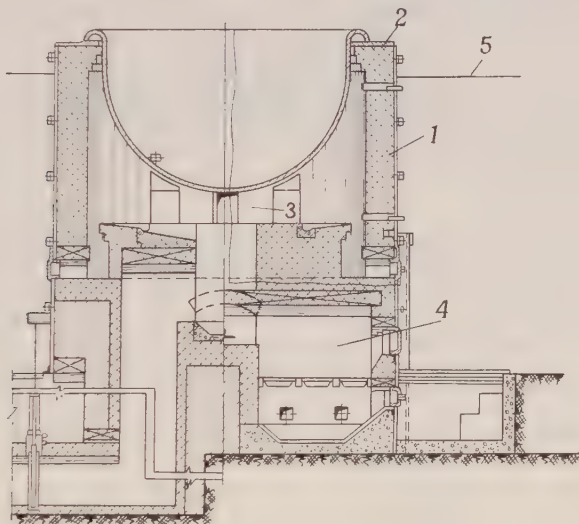


Fig. 110. Lead improving kettle:

1—brickwork setting; 2—mantle ring; 3—bottom supports; 4—firebox; 5—charge floor

gas or electricity. The kettle is built into a brickwork setting as shown in Fig. 110. The flue gases flow through a pipe round the kettle and are then discharged into a stack. An average refining kettle holds up to 200 tons of molten lead. Molten lead is poured into and withdrawn from the kettle by a centrifugal pump carried from kettle to kettle by an overhead travelling crane. Portable stirrers are used to mix the molten lead in the kettle (Fig. 111). Rotating at 100 to 160 rpm, the stirrer makes the lead circulate from top to bottom, forming a whirl on the surface of the molten metal. The reagents introduced into the whirlpool are entrapped by the stream of lead and are distributed well throughout the lead volume.

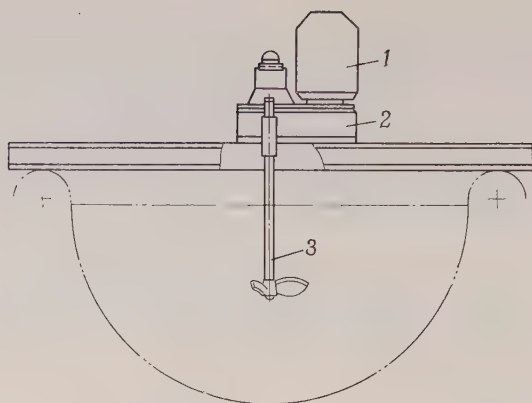


Fig. 111. Lead stirrer:
1—motor; 2—reduction gear; 3—stirrer

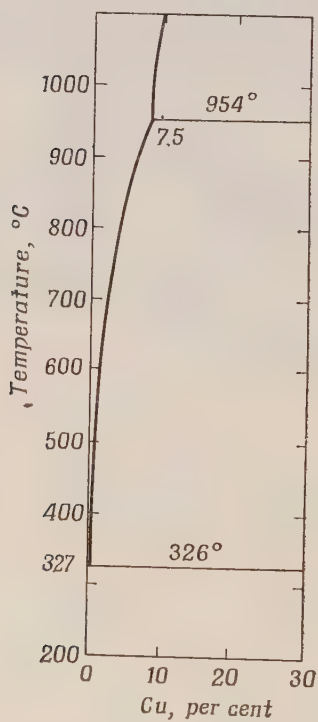


Fig. 112. Constitution diagram of the system Cu-Pb

Automatic temperature control would appreciably improve the refining operation and reduce refining costs, especially if electric heating is employed.

Copper removal. For copper removal, use is made of the reduction in its solubility with decreasing temperature, a technique known as liquation (or drossing). As the lead cools off, a solid solution of lead and copper with a specific gravity of about 9 separates out of it. The specific gravity of lead being 11.3, the crystals of the alloy, or the dross, rise to the surface.

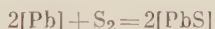
The percentage of copper removed increases with decreasing final temperature of the kettle. On the other hand, decreased temperature makes the molten lead less fluid, the dross slows down on its way to the surface, and the surface carries increasingly more molten lead.

Referring to the constitution diagram (Fig. 112), final solidification occurs at 326 C; the eutectic solidifying at this temperature runs 0.06 per cent Cu. It follows that the lowest temperature to which the lead may be allowed to cool in drossing should be above 326 C, and the least attainable copper content in such a case will be about 0.1 per cent.

In actual practice, the lead in the kettle is first allowed to cool slowly to 450°C, and the dross is removed from the surface of the lead with perforated ladles carried by overhead travelling cranes. At 450 C, the dross is powdery, carries relatively little molten lead, and is called dry. Its re-treatment will be described elsewhere in the book. Then the lead is pumped over into another kettle and is allowed to cool to 340-350°C. The dross produced now is a pasty mass carrying much molten lead. It is called wet and is returned to the first kettle.

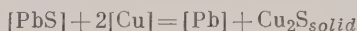
Both operations constitute what may be called primary copper removal. The copper content can only be brought down to 0.1 per cent. To carry copper removal further on, elemental sulphur is stirred into the molten lead at 330-350 C. The remaining copper reacts with the sulphur to form Cu_2S insoluble in lead. In settling, it rises to the surface as a dross. The dross of secondary removal consists of Cu_2S , PbS and mechanically entrapped droplets of lead and is skimmed off the surface of the molten metal with perforated ladles. Before a draw, the temperature of the lead is raised to 370 C so as to reduce the loss of lead with the dross.

Secondary copper removal is based on the formation of lead sulphide according to the reaction:



Why the PbS is preferentially formed will be clear from the law of mass action: the concentration of lead in the alloy is much

higher than that of copper. Lead sulphide dissolves in molten lead. As follows from the constitution diagram of the system Pb-S, the solubility of PbS at the temperature of the process may be as high as 0.7 or 0.8 per cent. Initially, the copper has a stronger affinity for sulphur than has the lead, and so:



Upon the attainment of equilibrium

$$K = \frac{a_{[\text{PbS}]} a_{\text{Cu}}^2}{a_{[\text{Pb}]}}$$

or, in view of the fact that $a_{[\text{Pb}]}$ is approximately equal to unity,

$$K = a_{[\text{PbS}]} \cdot a_{\text{Cu}}^2$$

Hence, the residual copper content of lead will be

$$[\text{Cu}] \approx a_{[\text{Cu}]} = \sqrt{\frac{K}{a_{[\text{PbS}]}}}$$

Putting it another way, the residual equilibrium concentration of copper after drossing will be the lower, the greater is the amount of PbS dissolved in the lead. For a saturated solution of PbS in lead (0.7-0.89 at 330-350°C), it amounts to a few millionths of one per cent, and the relevant requirements can be easily satisfied.

Sulphur consumption is about one part (by weight) to one part (by weight) of the copper removed, i.e., about 1 kg of sulphur per ton of lead.

The sulphide dross carrying 95 per cent Pb and 3 per cent Cu is usually returned for re-treatment, where it is added to the "wet" dross and charged into the first-over kettle.

The re-treatment of the copper-bearing dross is a separate operation.

The primary dross usually contains 50-80 per cent Pb and 10-25 per cent Cu. The quantity of dross drawn depends on the purity of lead bullion and usually ranges between 4 and 12 per cent of the lead weight.

The dross is melted in small reverberatory furnaces charged with green lead concentrate and iron scrap. The resultant matte is very high in copper and is disposed to copper smelteries where it is blown to blister copper in converters. The lead bullion produced is returned for "improving" or "softening". The slag is added to the lead charge smelted by the reduction process.

The removal of tin, arsenic and antimony by oxidation. Tin and antimony have a stronger affinity for oxygen than has lead (Table 33),

and their oxides are insoluble in molten lead. The two properties serve as the basis for the removal of these metals by oxidation.

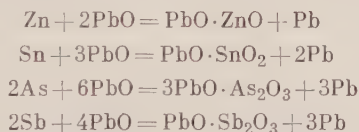
Table 33
**Heats and Standard Free Energies of Formation
for the Oxides of the Metals Removed from Lead
Bullion in Oxidation Improving (or Softening)**

Oxide	Heat of formation at 25°C, kcal/g-atom O	Standard free energy of formation at 25°C, kcal/g-atom O
ZnO	83.5	75.9
SnO ₂	66.5	61.7
Sb ₂ O ₃	55.0	49.9
As ₂ O ₃	52.0	45.3
PbO	50.7	44.9

The oxidation stage employs reactions and plant similar to those used in the fire refining of copper. The only difference is that lead oxide, as distinct from cuprous oxide, dissolves little in the metal being refined.

Oxidation is carried out in reverberatory furnaces at a temperature of 800-900°C.

Oxides of zinc, arsenic, antimony and tin are amphoteric. They are acidic with respect to PbO and form with it zincates, stannates, arsenites and antimonites:



The mixtures and alloys of these compounds removed from the surface of the bath are called skimmings.

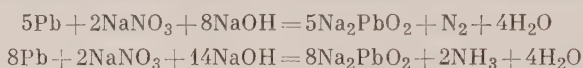
The rate at which the impurities are oxidised depends on their rate of diffusion towards the surface of the bath. The oxidation can be speeded up by blowing air through the molten bullion; the lead oxide forming on the surface of the rising bubbles reacts with the impurities while the bubbles are still rising to the surface. In addition, the air stirs the bath and promotes the diffusion of the impurities in the molten lead.

Of course, the precious metals are not oxidised during improving; but some of the gold and silver passes into the skimmings owing to the fact that the latter entrain droplets of lead which contain

dissolved gold and silver. The entrained lead can be partially sweated or liquated out of the skimmings, but the recovery is seldom satisfactory. Much lead passing into wastes, the difficulty of recovering the impurities in pure form, and the loss of the precious metals are the most serious drawbacks of oxidation. Some of the modern smelteries employ this principle only as a continuous process—a more sophisticated adaptation of the batch variety (see below).

Oxidation may use a stronger oxidant than oxygen, namely, sodium nitrate (NaNO_3), but the underlying principle remains the same—the utilisation of the difference between lead and impurities in their affinity for oxygen.

Coming in contact with a mixture of NaOH , NaNO_3 and NaCl , the molten lead is oxidised to litharge (PbO), and the litharge dissolves in the alkaline melt to form sodium plumbite:



The gases of this process mainly carry nitrogen for which reason the first reaction predominates.

The sodium plumbite oxidises the tin, arsenic and antimony owing to the fact that they have a stronger affinity for oxygen than has the lead.

In the alkaline melt, these oxides form respective oxysalts: Na_2SnO_3 , Na_3AsO_4 and Na_3SbO_4 .

The primary oxidation of the lead is due to the law of mass action, because its concentration is many times that of the impurities. Experience has shown that PbO does not accumulate in the melt until after the complete oxidation of all impurities, when it begins to pass into the melt at a high rate, giving it an orange-yellow colour. In other words, in this process PbO serves as a carrier of oxygen from the primary oxidant to the impurities.

Alkali-chloride improving (also known as the Harris process) becomes feasible at $420\text{--}450^\circ\text{C}$. Sodium chloride is added to NaOH because their mixture melts at a lower point than does NaOH alone.

Alkali-chloride improving is carried out in an apparatus shown in Fig. 113. It is an iron tank with a stirrer. The tank is mounted on a steel frame which also carries a pump to handle the lead and a feeder to introduce sodium nitrate. The whole apparatus is mounted on the top of a bullion kettle by a crane. The tapered portion of the tank dipped into the molten lead has a valve which only admits lead from the tank into the kettle.

After it has been warmed up, the tank is filled with a mixture of 3 parts of NaOH to one part of NaCl . The pump delivers lead

in a continuous flow over a riser into the tank whence it re-enters the kettle through the tapered bottom. Sometimes the stirrer may be dispensed with, for the pumping provides the necessary stirring

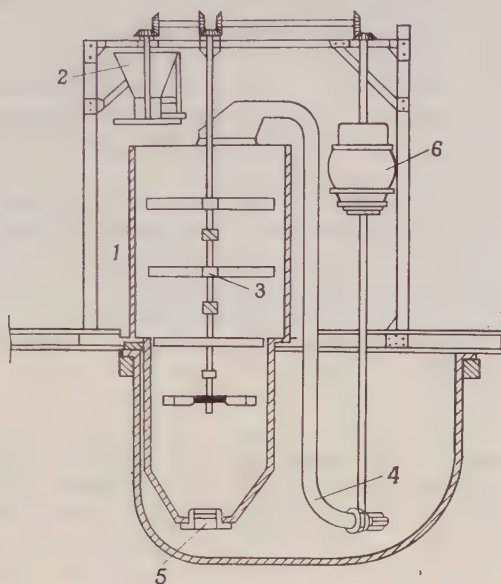


Fig. 113. Harris plant:

1—reaction tank; 2—sodium nitrate hopper; 3—stirrer; 4—pump; 5—valve; 6—motor

effect. The sodium nitrate is fed into the tank continuously throughout the operation. The reactions take place on the surface of the falling droplets of lead; the salts formed by the impurities remain in the melt.

The lead is passed through the tank until a sample taken from the kettle assays the required impurity content. Then the whole apparatus is transferred by crane onto another bullion kettle.

As it picks up ever more impurities, the alkaline melt grows thicker. When it has accumulated about 18 per cent As or 20 per cent Sn or 30 per cent Sb, it is tapped from the chemical treatment tank and is treated by a wet process for the recovery of the contained impurities and chemicals.

In treatment by a wet process, the molten alkalis are allowed to flow in a thin jet into a tank filled with water. The sodium hydroxide, sodium chloride, sodium stannate and sodium arsenate are dissolved, while the sodium antimonate and entrapped droplets of lead

settle to the bottom. After the residue is separated the hot solution is treated with lime to precipitate the calcium stannate which is then filtered off. In cooling, crystals of calcium arsenate separate out of the filtrate, and the remaining filtrate is evaporated to obtain a dry mixture of NaOH and NaCl which may again be used in the process for the refining of lead. The precipitated sodium antimonate separated from the lead droplets and containing up to 50 per cent Sb and under 0.2 per cent As + Sn + Pb is subjected to reduction smelting for the recovery of antimony. The stannate is smelted for tin. The arsenate is utilised in the manufacture of insecticides.

Alkali-chloride improving is free from the shortcomings of oxidation improving. The temperature of the process is low, and there are no losses of lead due to vaporisation. The impurities are more completely and separately recovered as rich salable products and can readily be reduced to metallic form. The losses of the precious metals are likewise negligible. Unfortunately, the process is fairly complicated.

In the absence of facilities for the recovery of the chemicals, their return to the process becomes impossible, and refining costs grow prohibitively high. Some refineries have modified the process by replacing the molten alkalis with solid chemicals. The reactions involved are the same, but the chemical treatment tank is simpler. It is an iron cylinder partly dipped into molten lead. There is a hole in the side of the cylinder through which sodium nitrate and alkali are introduced by hand. There is no stirrer, while the molten lead is continually pumped by two or three pumps. Alkali consumption is about half the amount required for working with molten reagents. The process is carried on at 500-550°C. The alkali first melts but then solidifies, as it becomes enriched with the impurities sought. Upon completion, the chemical treatment tank is removed, and the solid crust is skimmed off the kettle. Unfortunately, only a small proportion of the plumbite initially formed is utilised to oxidise the impurities, the trouble being in poor stirring. Furthermore, the solidifying alkali entraps up to 6 or 7 per cent metallic lead and the proportional quantities of gold and silver.

No successful methods have so far been developed for treating the caustic skims after lead improving with solid chemicals, and so the lead and impurities in the skims have to be regarded as lost. Against this background the straight Harris process using molten chemicals looks more attractive.

Desilverising and degolding. The separation of silver and gold from lead bullion is based on the fact that when 1 to 2 per cent zinc is stirred into a molten lead-bullion bath at 450°C (the Parkes

process), the zinc forms chemical compounds and alloys with gold and silver, all of them having melting points above that of lead:

Ag_2Zn_3	665°C
Ag_2Zn_5	636°C
AuZn	725°C
Au_3Zn_5	664°C
AuZn_3	475°C

Both the chemical compounds and solid solutions thus formed are lighter than lead and concentrate towards the surface of the bath where they can be removed as silver-zinc crust or dross.

The solubility of zinc in lead is limited (Fig. 114), and its excess also floats to the surface as a saturated solution of lead in zinc. Thus, a complex product consisting of gold, silver, lead and zinc is formed on the surface of the bath. The impurities As, Sn and Sb increase zinc consumption, retard the rising of the crust and may prevent a clean separation from the underlying lead. These drawbacks make obvious the importance of thorough improving (the removal of the three metals) prior to desilverising.

Desilverising and degolding are carried out in steel kettles. Zinc is stirred into a bath of molten metal with a mechanical stirrer in several additions, removing the crust with a perforated skimmer before every next addition. Thus, several crusts are skimmed during a single desilverising operation, progressively lower in doré silver, an alloy of gold and silver. The final skim carries only surplus zinc.

In order to obtain silver-zinc skims which are enriched, the previous day's blocks are added to the kettle of new, clean, improved lead. They are introduced at 480°C and, after the bath in the kettle is fully molten, are stirred mechanically for 20 or 30 minutes, and allowed to cool to 380°C when the first skim is removed. The same heating-cooling-skimming procedure is followed after every next addition.

The quantity of zinc necessary for the second and subsequent zincings depends on the amounts of silver and gold present which are determined by assaying a hot sample taken from the bath. Usually, it takes three zincings to remove silver down to 3 grams per ton. The entire cycle, including stirring-in of zinc, heating, cooling and skimming, takes up about 4 hours. Zinc consumption depends on the composition of the work lead (improved base bullion), and usually amounts to 1-1.5 per cent of the lead weight. Fuel consumption is about 3 per cent of the lead weight.

The silver-zinc crust is treated for the recovery of gold, silver, zinc and lead, the entrained lead being removed in suitable kettles by sweating or liquation (Fig. 115).

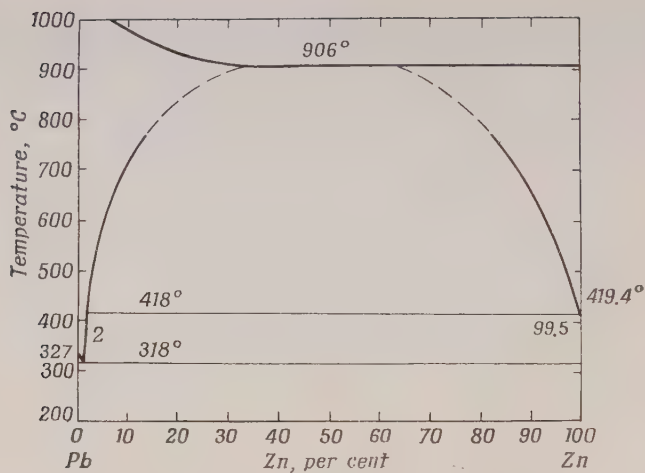


Fig. 114. Constitution diagram of the system Zn-Pb

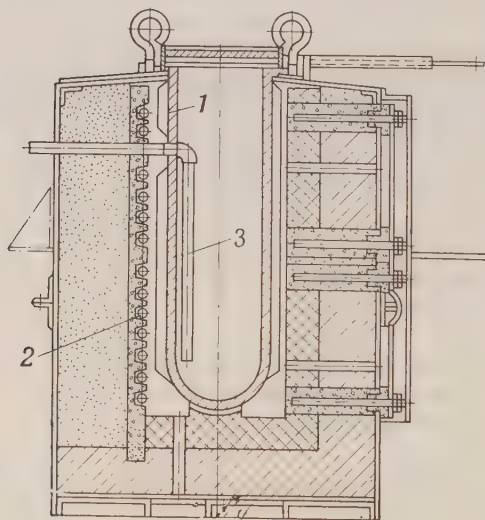


Fig. 115. Electrically heated liquation kettle:
1—kettle; 2—heater; 3—siphon tap

In a liquation kettle the crust is loaded over a stratum of molten lead heated to 650°C . The lead liquates out and trickles down a siphon tube into a receiver whence it is returned directly to the desilverising kettle. The dross left over from liquation is called the dry dross. The composition of the dry dross is given in Table 34.

Table 34

Approximate Composition of Silver-zinc Crust
(per cent)

Elements	1	2	3	4
Ag	10.69	10.4	14.0	22.6
Pb	75.54	55.5	44.0	50.0
Zn	10.7	22.0	40.0	20.0

The zinc in the crust is removed by retort distillation which utilises its greater volatility in comparison with lead and the precious metals. To this end, the crust is heated in a graphite retort (Fig. 116) for 5 to 8 hours at $1100\text{--}1200^{\circ}\text{C}$. Zinc vapours are withdrawn from the retort and condensed. To avoid the oxidation of the zinc, 3 or 4 per cent charcoal or anthracite breeze is added to the charge in the retort.

The lead left after dezincing assays 20-30 per cent doré silver and 0.7-2 per cent zinc; it is called rich lead and goes to the cupels for the recovery of gold and silver.

In addition to rich lead, distillation in retorts also produces some blue powder consisting mainly of zinc oxide and droplets of rich lead. The blue powder usually amounts to about 10 per cent of the charge weight. It is formed owing to the partial oxidation of the zinc during distillation; the zinc oxide and finely pulverised coal envelope the droplets of rich lead, thereby preventing them from coalescing.

A more recent trend in the Soviet Union has been to use the vacuum distillation process for dezincing. Using vacuum and electric furnaces, this process reduces distillation temperature, limits blue powder formation, and cuts down the loss of the precious metals, lead and zinc usually occurring in retort distillation.

The next operation in which rich lead is treated for the recovery of the precious metals is called cupellation. It consists in smelting the rich lead in a small reverberatory furnace at 1200°C while exposing it to a blast of air. The furnace is called a cupel (Fig. 117); hence the name of the process. The air blast oxidises the lead and

the base metals which are slagged off in the form of litharge. The litharge floats on the surface of the molten bath, while the doré silver remains beneath in metallic state.

After the cupel has been filled with doré silver, the residual lead is oxidised. The small quantity of litharge formed at the end of

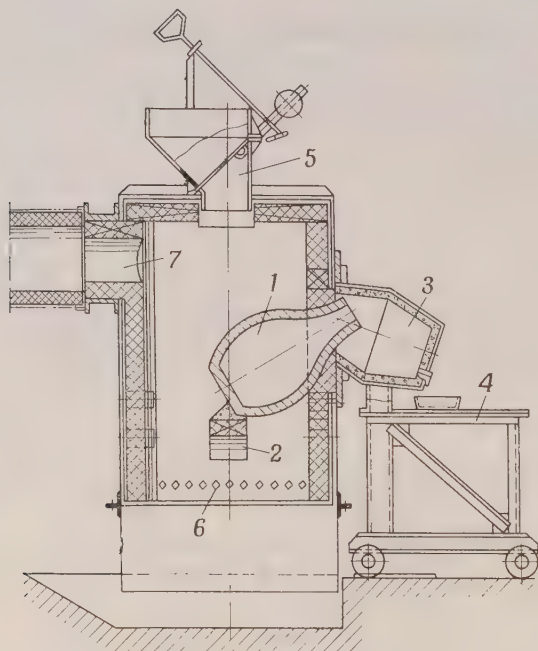


Fig. 116. Zinc-crust distillation furnace:

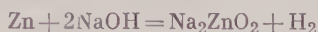
1—retort; 2—supporting arch; 3—condenser; 4—condenser support; 5—coke hopper;
6—grate; 7—gas flue

the cupellation is absorbed by the walls of the cupel. The doré silver is cast into moulds, and the bars constitute the finished product of a lead smeltery; their further treatment is carried out at silver refineries (see Chapter XI).

Dezincing. After desilverising, the lead carries 0.6-0.8 per cent Zn. The residual zinc can be removed either by oxidation, or by alkali-chloride fusion, or by vacuum distillation.

Oxidation is usually conducted in reverberatory furnaces where the residual zinc is converted, like tin, antimony and arsenic, into a skimming. This process involves considerable losses of lead and the precious metals.

Dezincing by alkali-chloride fusion (the Harris process) consists in treating the lead with an alloy of sodium hydroxide and sodium chloride in a chemical treatment tank described earlier (see Fig. 113). No sodium nitrate is required here as the zinc is oxidised with sufficient completeness by the caustic:



The operation commences at 350-360°C and attains completion at 460°C. The molten caustic carrying up to 30 per cent ZnO is then

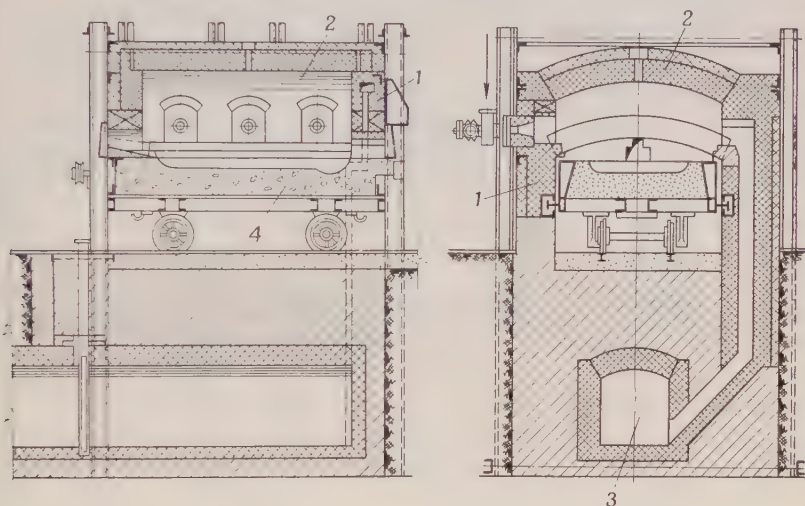


Fig. 117. Cupellation furnace:
1—wall; 2—roof; 3—flue; 4—draw-out cupel

allowed to flow in a thin jet into water; the oxysalts are dissolved, and the zinc oxide precipitates into a slurry. The slurry is filtered out, washed and dried; it contains up to 75 per cent ZnO and is suitable for the production of lithopone. The remaining liquor is evaporated, and the caustic is returned to the process.

Far better results are obtained when dezincing is done by the vacuum distillation process. The resultant zinc-lead alloy can be directly used instead of pure zinc in the removal of the noble metals from lead.

In the vacuum distillation process, the zinc is driven off at a temperature of 620°C and a vacuum of 0.2 mm Hg in an apparatus which is mounted on an ordinary kettle by crane. The frame of the apparatus mounts an up-turned steel hood with a water-cooled

bottom, connected to a vacuum pump (Fig. 118). As the hood is evacuated, the level of molten lead rises. The lead is pumped continuously by the vacuum-pump from the kettle through splashers into the vacuum space under the hood. Owing to the large aggregate surface area of the jets and droplets of lead, the zinc rapidly evaporates from it, and the zinc vapours are condensed as crystals on the

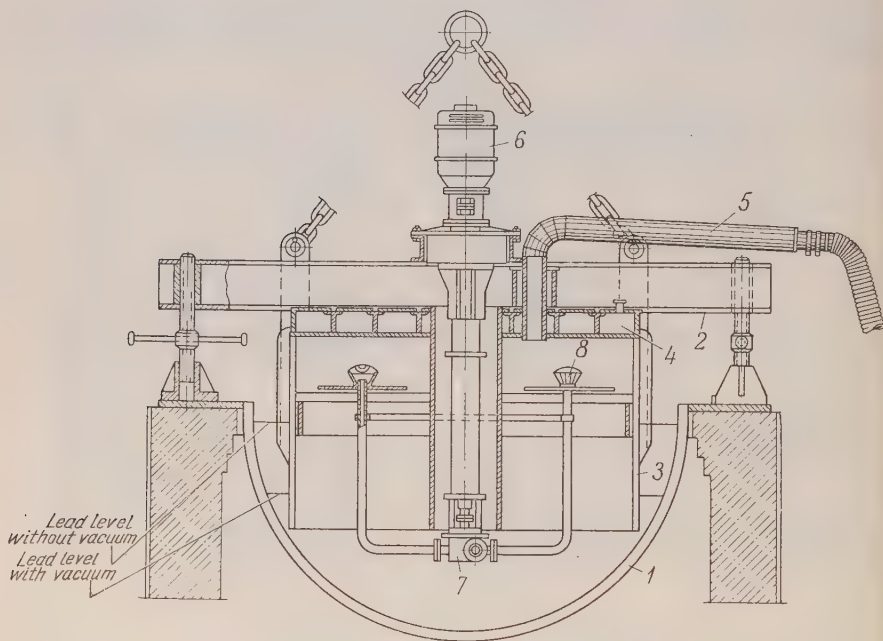


Fig. 118. Vacuum dezincing apparatus:

1--kettle; 2--support frame; 3--steel hood; 4--cooler; 5--to vacuum pump; 6--centrifugal-pump motor; 7--pump; 8--splashers

water-cooled bottom of the hood. After the dezincing operation, which lasts about 5 hours, the apparatus is dismantled from the kettle and is emptied of the condensate carrying 60 per cent zinc and 40 per cent lead. The refined lead contains not over 0.1 per cent zinc which is finally removed along with the magnesium and calcium (as described below).

Bismuth removal. Bismuth is removed by adding magnesium and calcium to dezincing lead at about 350°C (the Betterton-Kroll process). The two metals form with the bismuth chemical compounds and solid solutions insoluble in metallic lead and rising to the

surface of the molten bath. These compounds have the following melting points:

Bi_3Ca	507°C
Bi_2Ca_3	928°C
Bi_2Mg_3	715°C

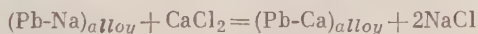
When used alone, calcium can only reduce the bismuth content to 0.05 per cent. When used jointly with magnesium, the bismuth content can be reduced to 0.008 per cent. The subsequent addition of some antimony brings down the bismuth content to 0.004-0.006 per cent by forming intermetallic compounds of the type Sb_xBi_y .

Magnesium is added to the lead in pig form, and calcium as a 3- or 4-per cent alloy with lead.

The magnesium and calcium are stirred into the molten lead in two additions. The first addition of three-fourths of the calculated amount is made, the bath is stirred for 30 minutes, and the first enriched bismuth dross is removed. Then, the balance of magnesium and calcium is added, and another dross removed. The first dross is treated for the recovery of bismuth, and the second is returned to the process for enrichment. After the surface of the molten bath has been cleaned of dross, finely divided antimony is introduced.

Bismuth drosses are smelted and cast into anodes. During electrolysis, the bismuth passes into the anode slime which is then melted to remove the metal.

The lead-calcium alloy required for debismuthising is prepared at the refinery. Direct alloying would cause much calcium to be oxidised; instead, a lead-sodium alloy is first prepared and is then treated with molten calcium chloride at about 700°C:



This technique is cheaper than direct alloying.

Removal of magnesium and calcium. After debismuthising, the lead carries excess magnesium, calcium and antimony as well as traces of zinc not removed by vacuum distillation. These impurities are removed in a single operation by alkali-chloride fusion (the Norris process), using a small quantity of sodium nitrate.

The refined lead is cast into moulds on casting wheels or straight-line machines.

Continuous processes. A major drawback of the batch variety of oxidation softening and desilverising is that the charge has to be cooled and reheated more than once, involving increased expenditures of time and fuel and reducing overall efficiency.

Some refineries employ a continuous process in which the removal of tin, antimony and arsenic (or softening) as well as of silver and gold (desilverising and degolding) is conducted uninterrupted,

while the copper is drossed and the bismuth is eliminated intermittently.

The arsenic and antimony are removed in a continuous softening furnace of the reverberatory type by oxidation. Lead is fed into and

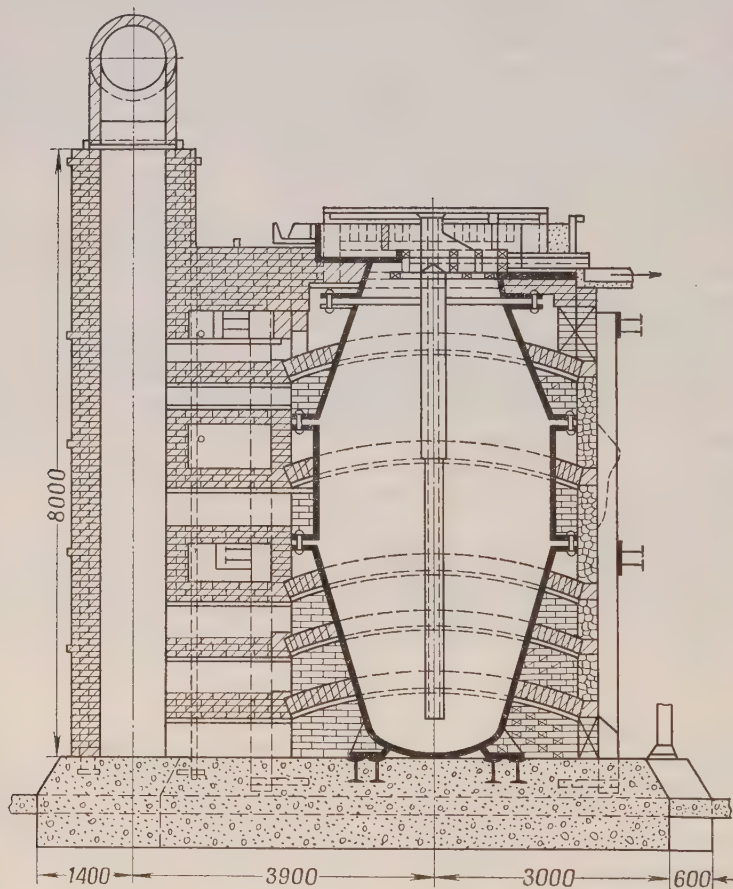


Fig. 119. Continuous desilverising kettle

withdrawn from the furnace in a continuous flow. In the furnace, the molten lead is blown with air from submerged perforated iron pipes. The intensive stirring and the self-catalytic nature of the reaction serve together to speed up the oxidation of the impurities; the relatively large quantity of PbO formed dissolves the oxides and floats to the surface to be slagged off continuously. The furnace is

driven at 750°C which is often attained without any extraneous fuel, for the oxidation of the lead impurities is exothermic. Passing through one or two softening furnaces operating in tandem, the softened lead bullion enters the continuous desilverising kettle.

The kettle (Fig. 119) is a barrel-shaped unit of cast iron. When operating, the kettle is filled with lead covered by a layer of molten zinc 1 metre deep. The kettle is placed into a brickwork setting so arranged that there are several independent heating chambers, and any portion of the kettle may be heated as required: the lower lead stratum to about 330-340°C, the zinc to 600°C, and the middle portion to a temperature gradually changing between the two limits.

As lead bullion flows in, its contact with the zinc causes progressive enrichment of the zinc in the compounds of the type Ag_nZn_m . The lead moves downwards in the kettle; in passing down the temperature falls, a zinc-silver crust separates from the solution and rises to the surface. The desilverised lead reaches the bottom whence it passes up the siphon pipe placed centrally in the kettle and flows freely to a continuous dezincing unit. When the zinc layer has reached the desired enrichment in silver and gold, which occurs at least twice every twenty-four hours, it is hand-ladled to bars, and the zinc layer is immediately built up again with fresh zinc. The zinc-silver crust assays 15-20 per cent Ag, 15 per cent Pb and 65 per cent Zn. Its doré silver content is much higher than in the case of batch desilverising.

Dezincing is conducted in reverberatory furnaces by producing molten slag which mainly contains litharge.

In terms of its antimony, zinc and silver contents, the refined lead obtained by the continuous process meets the requirements of the relevant U.S.S.R. State Standard for Grade C2.

The hourly output of the continuous desilverising unit incorporating the kettle, shown in Fig. 119, is 30 tons which is upwards of what can be attained with batch desilverising.

The other advantages offered by the continuous process in addition to high capacity are low fuel consumption, the possibility of mechanising and automating the process, and the high content of the precious metals in the zinc crust.

Electrolytic Lead Refining. The best grades of electrolyte for lead refining are those containing amidosulphonic and phenol-sulphonic acids. Their commercial utilisation, however, has not yet reached any appreciable degree, and many refineries continue to use fluosilicic electrolyte.

This electrolyte is a colourless liquid composed of about 9 per cent Pb as $PbSiF_6$ and 8 per cent free fluosilicic acid (H_2SiF_6). During electrolysis, the electrolyte is not practically contaminated

and requires no purification. Its mechanical losses amount to 3 or 4 kg of acid per ton of lead.

The anodes are cast of lead bullion or resmelted bismuth skimming. They are the same shape as for copper refining, weighing 125-250 kg and measuring 600-900 mm in length and 500-600 mm in width; their thickness is about 40 mm. The size and weight of anodes should be reduced for lead bullion high in impurities.

The cathodes or starting sheets are made of pure lead 3 or 4 mm thick and are somewhat larger than the anodes.

Electrolysis is conducted in concrete tanks lined with asphalt or plastics. Usually 20 to 24 anodes and one more cathode than anodes are placed in a tank.

The anodes usually remain in the tank from 10 to 15 days, while the cathodes are removed at the end of 5 days and smelted to refined lead.

As the anodes dissolve, only the lead, zinc and tin pass into solution. The other impurities sink to the bottom of the tank as a strong porous slime crust. Electrolyte circulation through the pores of the slime grows increasingly difficult, the anode potential rises rapidly due to the voltage drop across the slime, and other impurities notably antimony may pass into solution. To avoid this possibility, the lead before it is cast into anodes is given oxidation softening, and the slime crust is regularly scraped off the anodes during electrolysis. Special emphasis is usually placed on the removal of copper prior to electrolysis, as its presence in the anodes speeds up polarisation. The antimony content of the anodes may be as high as 7 to 11 per cent without causing any appreciable adulteration to the electrolyte.

The deposition of impurities at the cathodes is mainly due to the mechanical entrainment of electrolyte and fine particles of the floating slime. Anodes from resmelted bismuth skimmings give a low-quality cathode lead which has to be re-refined pyrometallurgically.

The current density to use is chosen according to the composition of the anodes and usually ranges between 125 and 200 A/sq m, being lower for anodes containing more impurities.

The temperature of the electrolyte is maintained at 35 to 40°C. The initial voltage across the tank is 0.4 V, but it rises to 0.8-1 V due to polarisation as the slime deposit increases.

Power consumption for a current efficiency of 97-98 per cent is but 110 kWh/ton due to the high equivalent weight of lead.

The anode slime is collected, washed and smelted in reverberatory furnaces. The furnace treatment of anode slime volatilises all arsenic and considerable antimony which pass off with flue gases as oxides. The remaining metal is further oxidised to remove the remaining

antimony, tin and zinc and is then cupellated. The cupellation causes the bismuth to pass into litharge, and only doré silver is left in the cupel. The litharge is re-treated for the recovery of bismuth.

The slime produced from anodes cast from bismuth skimmings carries 60-70 per cent Bi and very small quantities of other impurities. It can be conveniently re-treated for the recovery of bismuth to a high degree.

Electrolytic refining is more advantageous than furnace refining. It produces 96-98 per cent market lead from the crude grade while in furnace refining the figure is 75-80 per cent, the wastes accounting for as much as 25 per cent lead.

Yet, furnace refining continues to dominate the field owing to the toxicity of the electrolyte and the difficulties involved in slime treatment.

70. Extraction of Cadmium and Other Metals from Lead Concentrates

Referring to Table 30, the flotation of lead-zinc ores produces lead concentrates which contain some quantity of cadmium, indium, thallium, etc.

During roasting, sintering and smelting, the cadmium and trace metals concentrate in the flue dust. Their contents, in per cent of their amounts in the original concentrate, are as follows:

Cd	Tl	Se	Te	In
73	73	50	50	17

These amounts are large enough to warrant the treatment of lead-smelting dust for the recovery of not only cadmium, as has been noted elsewhere, but also of thallium, selenium and tellurium.

Of this amount, up to 80 per cent indium passes into slag in blast-furnace smelting. In drossing, it concentrates in the copper dross, forming indium arsenides and antimonides and solid solution in copper. The copper dross also carries much selenium, cadmium and germanium. Both the slag and dross may also be treated for the recovery of these metals.

Chapter IX

THE METALLURGY OF TIN

71. General

Tin is known to exist in three allotropic modifications. In its normal state, known as beta-tin, it is a silvery white, lustrous and extremely malleable metal with a density of 7.3 g/cu cm. This modification remains stable from 13°C to 161°C. When heated to above that point, the metal changes to gamma-tin with a density of 6.5 g/cu cm; it is very brittle and readily disintegrates to a fine powder.

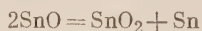
Below 13°C, alpha-tin exists, having the crystal structure of diamond and a density of 5.85 g/cu cm. The transformation of beta-into alpha-tin is accompanied by a sharp reduction in density and the metal spontaneously changes to grey powder. Near the temperature of transformation the rate of change is low, but it increases with decreasing temperature and reaches the peak at -45°C. This transformation is called tin disease or pest and makes impossible the use of tin articles at extremes of cold such as occur in the Arctic or the Antarctic. Incidentally, the destruction of the tin-soldered fuel tanks was one of the causes why Captain Scott's expedition perished in the Antarctic in 1912.

Resmelted in conditions which prevent oxidation, such as under a blanket of rosin, the grey powder of alpha-tin easily changes to a plastic metal.

Tin melts at 231.86°C and boils at 2270°C. It has a low hardness and a low strength, high electrical and thermal conductivity.

Tin can be bi- and tetravalent. It has an electrode potential of -0.136 V and a high hydrogen overvoltage, for which reason it dissolves slowly in diluted hydrochloric and sulphuric acids. At heating, strong hydrochloric acid readily dissolves tin, and the ions Sn^{2+} formed in the process are an efficient reducing agent.

At normal temperature tin is stable both in air and in water, its oxidation becoming noticeable only above its melting point. At elevated temperatures tin is oxidised to stannic oxide (SnO_2) which is a non-fusible white powder. The vapour pressure of SnO_2 is 760 mm Hg at about 1850°C. In metallurgical melts, this oxide has the properties of a weak acid. On the other hand, stannous oxide, (SnO), has the properties of a base, but is stable only in alloys with other oxides, i.e., in slag. At above 370°C, free SnO undergoes a slow change:



SnO is appreciably volatile, and its boiling point is estimated at about 1425°C .

Molten tin readily alloys with other metals, forming a strong film on their surface—the basis of its uses in soldering. The same property is utilised in the manufacture of tin plate widely used for canned foods. At present, about half the tin produced is utilised for that purpose. Tin also goes to coat utensils and chemical apparatus as a protection against corrosion.

Large quantities of tin go to make bronzes; average tin content of bronzes is however much lower than was the case in the past, tin being replaced by zinc and lead (Soviet Grades OII and OIIC).

Tin is the base of babbitt metals which are alloys of tin, copper, antimony, and some other elements. Tin also makes part of type metals and several other alloys. Stannic oxide, SnO_2 , still finds use as an opacifier in glazes and heat-resistant enamels.

Still, in comparison with other heavy non-ferrous metals, world production of tin is on a modest scale.

72. Tin Ores

By far the most important ore of tin is the mineral cassiterite (or tin stone), which is tin dioxide (SnO_2). The specific gravity is from 6.8 to 7.1, and the colour is from light-yellow to brown, depending on the nature and content of impurities. Sulphide tin ores sometimes carry another mineral, stannite, which is a triple sulphide of tin, copper and iron ($\text{Cu}_2\text{FeSnS}_4$).

Cassiterite is the commercial ore which occurs either in original deposits in the form of veins or lodes (hence the term "vein tin" or "lode tin"), and also in transported alluvial or placer deposits (called "stream tin").

Furthermore, vein or lode tin may be classed according to the size of cassiterite grains and the type of gangue. In fine-grained ores cassiterite is present as particles measuring from 0.001 to 0.2 mm across, and in coarse-grained varieties as particles from 2 mm upwards.

The metals often found associated with cassiterite in lode deposits are tungsten, sometimes lead, zinc and copper, in some cases the minerals of tantalum, niobium, titanium, beryllium, indium, rare earths and scandium.

Tin ores usually contain not more than 1 per cent Sn. Placer ores are commercially attractive with a lower tin content than lode deposits (down to 0.01 or 0.02 per cent tin) because they are easier and cheaper to mine with open cuts, hydraulic sluicing and dredging.

Tin is not extracted from ores directly. In most cases, tin ores are beneficiated to obtain concentrates with 40 to 70 per cent tin. Dressing is conducted on jigs, concentrating tables, and by flotation.

Magnetite, tungstate and other magnetic minerals can be separated from cassiterite by magnetic separation.

The tin content of concentrates depends on its content in the original ore and the grain size of cassiterite. In the case of fine-grained ores, even though they may be high in tin, the resulting concentrate will contain from 50 to 60 per cent tin, while the figure rises to 70 or 87 per cent for leaner ores but containing large cassiterite grains. The composition of several tin concentrates, in per cent, follows:

Sn	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	S	Cu	Pb
60	11	6	3	3	0.2	0.4
50	17	9	5	4	0.2	0.4
40	19	11	7	6	0.5	1.2

73. Preparing the Ore for Smelting

As often as not tin concentrates have to be treated specially so as to remove the metal impurities they contain and make them suitable for smelting. The actual methods of concentrate purification and treatment depend on the analysis of a given ore and may sometimes be very complicated. In some cases, the treatment may be limited to roasting, in others roasting may be followed by leaching or magnetic separation, in still others a combination of these methods may be employed.

Roasting. Roasting is used to remove sulphur, arsenic and antimony. The sulphur content of concentrates, especially from lode ores, may be as high as 5 per cent. It should be eliminated to the fullest possible extent, for sulphur causes tin to volatilise during smelting as SnS. The contents of arsenic and antimony in lode tin concentrates often amount to 5 per cent and 2.5 per cent, respectively.

Sulphur elimination by roasting may be fairly complete (down to a few hundredths of one per cent), but this requires high temperatures, a long dwell of concentrate in a roaster or furnace, thorough rabbling and, sometimes, grinding prior to roasting.

Arsenic elimination by roasting is based on the formation of volatile As₂O₃. Unfortunately, arsenic elimination is hampered by oxidation to As₂O₅ which produces arsenates. This condition may be prevented by adding some coal to the charge prior to roasting, but it slows down the burning of sulphur. In any case, it is extremely difficult to obtain a calcine containing less than 0.1 per cent As. Accordingly, roasting is carried on until the bulk of the arsenic content is removed, the balance being eliminated by subsequent acid leaching.

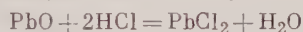
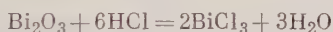
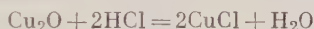
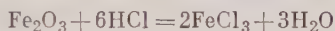
Antimony is still more difficult to remove by roasting than arsenic. Its sulphides are oxidised to form predominantly almost non-volatile Sb_2O_4 .

The impurities Pb, Bi, Cu and Zn are converted by roasting from sulphides to oxides some of which form ferrites and silicates with Fe_2O_3 and SiO_2 .

The roasting of tin concentrates is done in mechanical multiple-hearth revolving-rabble type roasters or in rotary kilns. The roasting temperature is anywhere between 600°C and 700°C , and 1 to 2 per cent coal is added to the green concentrate.

Leaching. In most cases, leaching follows roasting, because sulphides react with acids less readily than do oxides. Furthermore, roasting prevents the formation of toxic hydrogen sulphide.

Leaching uses a 28- to 30-per cent solution of hydrochloric acid and proceeds according to the following reactions:



Hydrochloric acid is added with some excess in order to speed up leaching and to prevent the hydrolysis of the salts.

If the impurities Fe, Pb and As are to be leached out to the extent of 85 to 95 per cent, a temperature of about 130°C has to be maintained, for which reason leaching is usually done in autoclaves (Fig. 120).

On the inside an autoclave is coated with rubber and then lined with acid-proof brick. The live steam required for heating is admitted through a hollow trunnion. The solution obtained by leaching is treated on intermittent-type vacuum filters with PVC filtering elements. Before they are discharged into sewers, the effluents are neutralised by lime; the hydroxides and basic salts that precipitate as a result of this treatment are recovered by filtering. If the precipitate carries much bismuth or other valuable metals, it is retreated for their recovery.

Leaching is often followed by magnetic separation in order to remove the magnetite and tungstate contents of the tin concentrate. Leaching with hydrochloric acid removes the oxide film from the grains of cassiterite, and disk-type magnetic separators divide the charge into a strongly magnetic fraction (magnetite), a weakly magnetic fraction (tungstate), and a non-magnetic fraction (cassiterite).

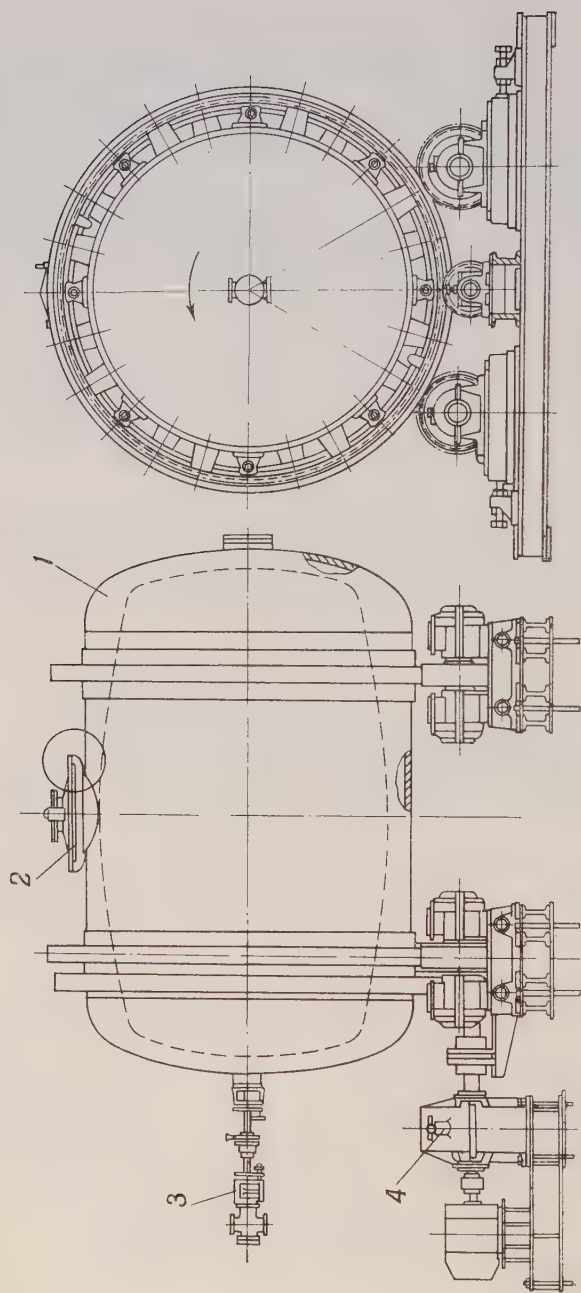


Fig. 120. An autoclave for tin concentrate leaching:
 1—shell; 2—hermetically sealed cover; 3—steam in; 4—rotating mechanism

Sometimes leaching is preceded by heating the concentrate with sodium carbonate. The reason is this. Some tin concentrates contain tungsten compounds which are not greatly affected by ordinary roasting. When these compounds are heated with sodium carbonate, sodium tungstate is formed, easily soluble in water and may be removed by leaching with water, while the cassiterite of the concentrate remains unaffected.

74. Extraction of Tin

From concentrates tin is extracted solely by pyrometallurgical methods. The hydrometallurgy of tin has not found any appreciable application because cassiterite is practically insoluble even in concentrated solutions of acids and alkalis.

Of all pyrometallurgical methods, the oldest and most commonly used one is carbon reduction—the tin concentrate is smelted in a charge containing coal and flux to pig tin and slag. Smelting may be done either in reverberatory or electric furnaces.

The principal difficulty in reduction smelting is the separation of tin from iron. The smelting conditions should be such that the tin oxide is reduced to the metallic state, while the iron oxide is reduced only to ferrous oxide and passes into the slag.

Tin has a weaker affinity for oxygen than has iron; yet, at the temperatures required to produce liquid slags some of the iron does change to metallic form. The reduction of some iron is further facilitated by the formation of FeSn and FeSn_2 . Therefore, pig tin is always contaminated with some iron.

Copper, antimony, arsenic, bismuth and lead have a weaker affinity for oxygen compared with tin; therefore, in reduction smelting they are reduced and dissolved in pig tin.

The refining of tin produces a considerable quantity of tin-bearing wastes. By way of example, the removal of iron down to 1 per cent may cause 3 to 6 per cent tin to pass into the iron dross.

In order to control the reduction of iron, smelting has to be conducted in a moderately reducing atmosphere with the result that a fairly large quantity of tin fails to be reduced to metallic form; instead, the tin oxide combines with silica and goes into the slag. The amount of tin contained in practically all first-run slags is so high that they have to be re-treated for their tin content.

A simplified flow-sheet for the smelting of tin from concentrates is shown in Fig. 121.

Reduction smelting is not applicable to very low grades of tin concentrates, concentration middlings, tin ores and other materials low in tin. Research work is therefore under way to find alter-

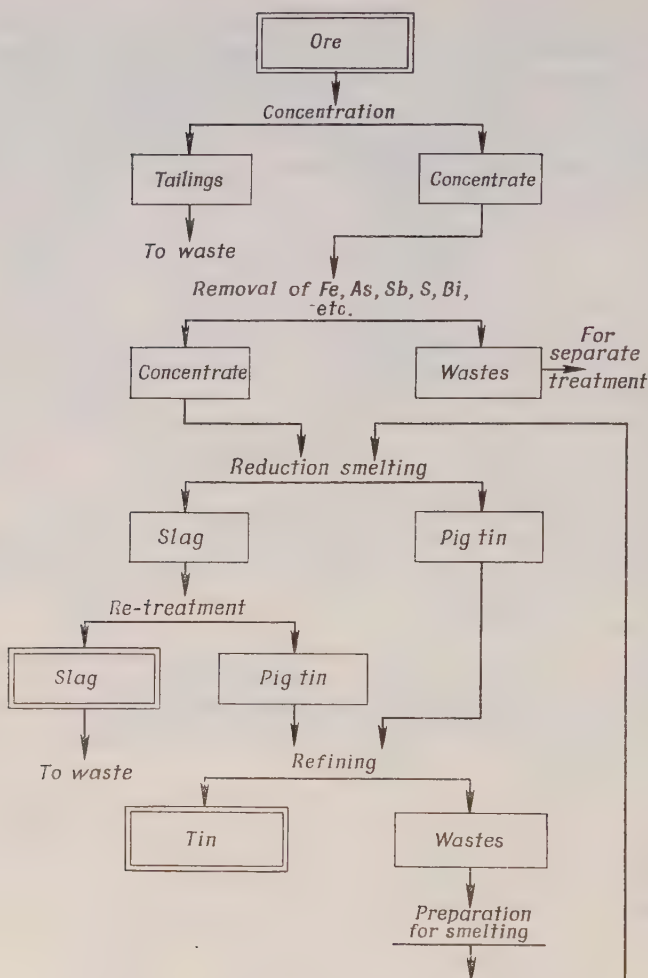
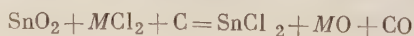


Fig. 121. Flow-sheet for the reduction smelting of tin concentrates

native methods of tin extraction from them. One of such methods is the chloridising process.

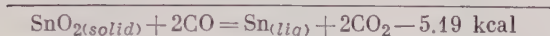
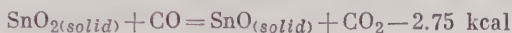
The chloridising process is based on the considerable affinity of tin for chlorine and the volatility of tin chlorides. The tin-bearing material is mixed with chlorides of iron or calcium and heated in a reducing atmosphere at about 800°C. The tin is chlorised according to the reaction:



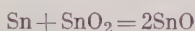
The tin chloride is condensed, while its fumes are caught by dust catchers. From the chloride, the tin is extracted by electrolysis.

75. Primary Smelting

The primary smelting of tin proceeds in two stages:

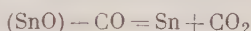


Some of the stannous oxide has no time to be reduced to metallic form and passes into the slag. Some SnO may also be formed as follows:



The bulk of the iron is reduced to FeO and enters the slag.

The reduction of the stannous oxide dissolved in the slag may be thought of as proceeding as follows:



$$K = \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \cdot \frac{a_{(\text{SnO})}}{a_{[\text{Sn}]}} ,$$

where $a_{(\text{SnO})}$ is the activity of tin oxide in the slag and $a_{[\text{Sn}]}$ is the activity of tin in the pig metal.

The equilibrium vapour pressure of CO in a gas mixture increases with decreasing activity of tin oxide in the slag.

The reduction of ferrous oxide in the tin-smelting slag is facilitated by the dissolution of iron in metallic tin. The free energy of iron reduction in this case is increased by the free energy of iron solution in tin and the free energy of formation of the accompanying chemical compounds.

For the reaction $(\text{FeO}) + \text{CO} = [\text{Fe}] + \text{CO}_2$ we similarly find that

$$K_{\text{Fe}} = \frac{p_{\text{CO}}}{p_{\text{CO}_2}} \cdot \frac{a_{(\text{FeO})}}{a_{[\text{Fe}]}} ; \quad \frac{p_{\text{CO}}}{p_{\text{CO}_2}} = \frac{a_{[\text{Fe}]}}{a_{(\text{FeO})}} \cdot K_{\text{Fe}}$$

From this relationship it follows that given a constant composition of gases, the quantity of iron passing into tin will increase with increasing activity of FeO in the slag. The composition of gases present in the charge depends on the equilibrium of the reaction $\text{C} + \text{CO}_2 = 2\text{CO}$ at the temperature of smelting. It is the same for both tin and iron; consequently:

$$\frac{p_{\text{CO}}}{p_{\text{CO}_2}} \cdot \frac{K_{\text{Sn}}}{a_{(\text{SnO})}} = \frac{a_{[\text{Fe}]}}{a_{(\text{FeO})}} K_{\text{Fe}}$$

or

$$\frac{K_{\text{Fe}}}{K_{\text{Sn}}} = \frac{a_{(\text{FeO})}}{a_{(\text{SnO})} \cdot a_{[\text{Fe}]}}$$

The equilibrium constants K_{Sn} and K_{Fe} give a measure of the affinity of the two metals for oxygen. Iron has a stronger affinity for oxygen than has tin, and so tin may be reduced from the slag more than can iron.

Experience shows that at the elevated temperatures of smelting, almost all tin and iron is reduced from the slag in electric furnaces. In reverberatory furnaces, considerable quantities of tin do remain in the slag.

The reduction of tin and iron also depends on the acidity of the slag. In the case of acid slags, the activities of SnO and FeO are lower than with basic slags. An addition of calcium oxide to the charge enhances the reduction.

The furnaces employed for tin smelting must permit of simple and reliable temperature control and slag superheating for the complete recovery of tin. Blastfurnaces do not meet these requirements. Furthermore, the charge column in blast furnaces is blown with a strong blast which promotes the volatilisation of SnS and SnO.

On the other hand, both temperature and gas composition are easy to control in reverberatory furnaces. Still better results are obtained in electric furnaces. In the latter, the smelting space is hermetically sealed, there are no fuel gases present, and so the dust losses may be kept to a minimum. Furthermore, electric furnaces may be run at considerably higher temperatures than reverberatories, which fact permits the use of high-melting slags high in lime and a more complete reduction of tin. Though cleaner than blast-furnace slags, those from reverberatories have to be resmelted in order to recover their tin content. On the other hand, electric-furnace slags may often go to dumps directly. It should be added, however, that electric-furnace smelting is only good for tin concentrates very low in iron, since at the very high temperatures maintained in electric furnaces almost all iron in the slag is reduced to the metallic state.

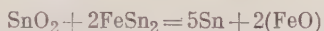
Tin-smelting reverberatory furnaces are similar in design to those used for copper refining.

The crucible is built of magnesite brick placed in an iron shell which is supported by columns for the better cooling of the shell; in this way the leakage of high fluid molten tin through the joints in the brickwork is prevented. The bottom is inclined towards the side wall where tap holes for tin and slag are placed. The fuel may be either fuel oil, gas or pulverised coal fed through burners located in the front end. Pulverised coal is less desirable because the ash

increases the quantity of slag; in addition, coal always contains sulphur which may cause losses of tin in the form of volatile SnS .

Fig. 122 shows a reverberatory furnace with a hearth area of 22.3 sq m. Reverberatories with a hearth area of up to 40 sq m are also built. The furnace is adapted for the charge to be introduced through openings in a side wall and for smelting without rabbling.

The charge consists of tin concentrate, light coal and lime which are mixed in mechanical mixers and moistened to 7 or 8 per cent to reduce tin losses with dust. An overhead travelling crane feeds the charge into hoppers over the furnace from which it flows into the crucible to form banks at the side walls. The furnace is run at 1150-1200°C, and a single batch is smelted for 6 hours. At the end of a smelting period, the furnace is tapped before a second charge is put in. The reduced tin is allowed to flow into a steel settler. On cooling, crystals of FeSn_2 separate out on the surface to be removed with skimmers as a crust and returned to the furnace. Some tin smelteries separate the FeSn_2 dross by passing the molten tin through a coke filter at about 500°C. The reduced iron is returned to the furnace where it is oxidised by the cassiterite and passes into the slag:



The daily output of reverberatory furnaces is up to 1.8 tons of tin concentrate per square metre of hearth area. Fuel consumption is about 0.3 ton per ton of charge. From 50 to 90 per cent of the tin contained in the source concentrate is withdrawn into pig tin, the actual figure depending on the Sn/Fe ratio in the concentrate.

Reverberatory-furnace slags usually have the following composition (in per cent):

Sn	SiO_2	FeO	CuO	Al_2O_3
4-12	22-24	17-22	14-15	12-14

The tin carried by the slag is present as stannous oxide and droplets of entrained tin. The quantity of entrained tin increases with increasing specific gravity and viscosity of the slag. Droplets of tin are also caught by the slag owing to the fact that the slag does not wet them properly and they are carried by gas (CO_2) bubbles to the upper layers of the slag. Some tin also disperses throughout the slag.

Opinions as to which slag is the best differ. In most cases, slag calculations are based on a pH value of 1.25-1.5 (less Al_2O_3) and a molar ratio of FeO to CaO equal to unity.

The dust carried off with the flue gases is caught and returned to the furnace. This is done by cooling the gases in scrubbers and by passing them through electrostatic precipitators. The scrubber

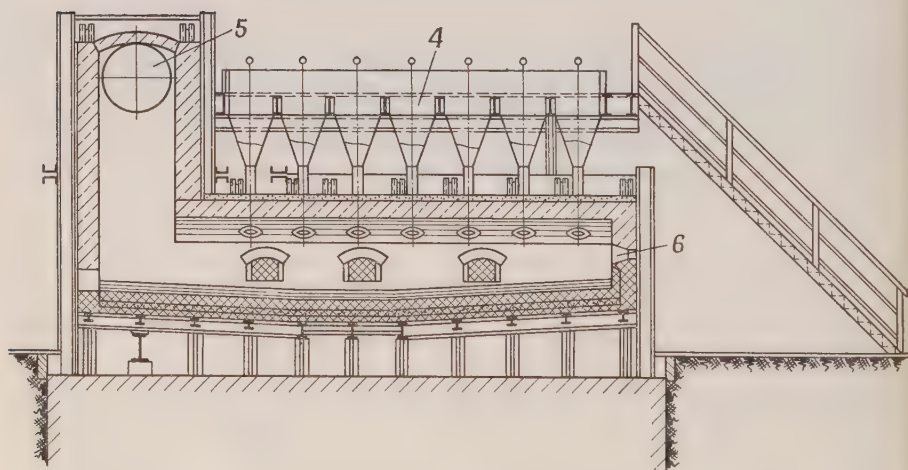
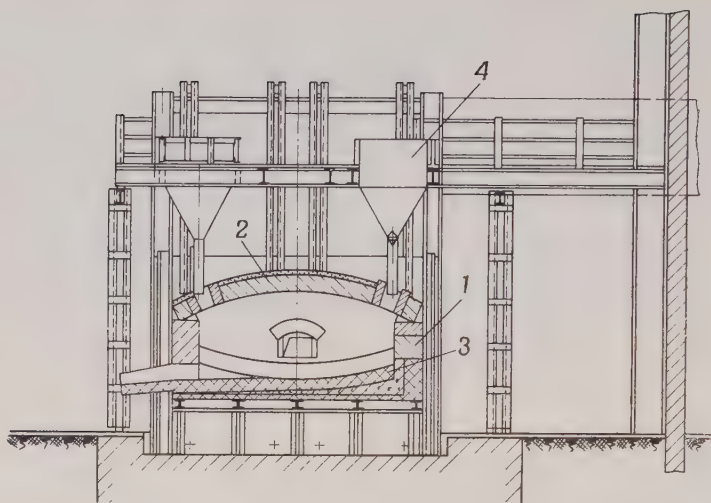


Fig. 122. Reverberatory tin furnace:

1—walls; 2—roof; 3—hearth; 4—charging hoppers; 5—flue; 6—burner ports

slime may contain from 40 to 50 per cent tin, while the dust from electrostatic precipitators may carry up to 60 per cent tin. The dust losses of tin account for 8 to 12 per cent of the tin in the charge. The flue dust also collects the impurities As, Sb, Pb and other metal, notably indium which is carried off as In_2O fumes.

Higher daily outputs (up to 4.5 tons per square metre) are attained with electric furnaces.

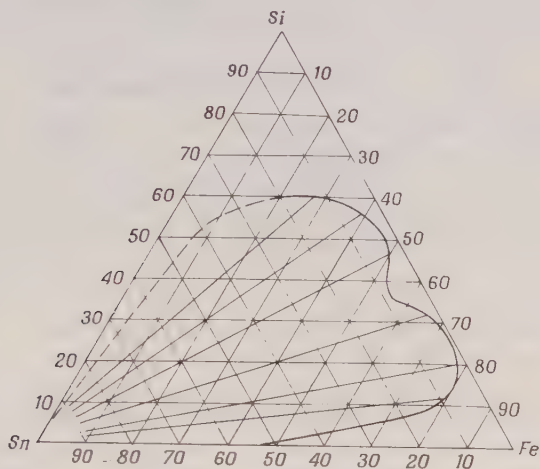


Fig. 123. Three-component diagram, Sn-Fe-Si, showing the zone of separation (after Murach and Likhmitskaya)

Tin-smelting electric furnaces are similar to those employed for steelmaking, but are built stationary. Three graphitised electrodes are passed through the roof into the smelting space so that their ends are dipped in the charge. The phase voltage is 120 to 130 V. The temperature in the furnace is maintained automatically by lowering or lifting the electrodes. A single charge is smelted during six hours, and power consumption is about 1650 kWh per ton of tin. The tin content of electric-furnace slags is from 0.2 to 1 per cent. About one-third of all the slag produced carries less than 0.3 per cent tin and goes directly to the dump.

When SiO_2 is used as flux in electric-furnace smelting, tin concentrates high in iron (up to 3 per cent Fe) may be processed. The silicon reacts with the iron to form ferro-silicon which forms a separate liquid stratum between the tin and the slag.

Fig. 123 shows the equilibrium diagram of the system Fe-Sn-Si from which it is possible to calculate the requirements in silicon for the production of a ferro-silicon which is the lowest in tin.

Silicon or rich ferro-silicon is charged two hours before the end of the heat. After the heat, the furnace is tapped, and its content is allowed to flow into a settler lined with graphite blocks. The tin and ferro-silicon remain in the settler, and the slag overflows into a slag pot. When it solidifies, the ferro-silicon is removed from the settler by an overhead crane. It contains 24-26 per cent Si and 2.5-3.5 per cent Sn. For concentrates very high in iron, silicon smelting is not attractive because of high silicon consumption and considerable losses of tin in the ferro-silicon.

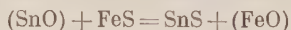
76. Resmelting of the First-run Slag

A slag may go to the dump only if its tin content is not over 0.3 per cent, which is obviously not the case with the first-run slags of tin smelting. This fact necessitates their resmelting.

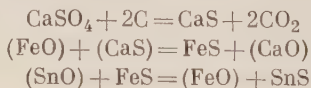
One of the best methods for re-treating the first-run slag is to smelt it in an electric furnace with the proper addition of a reducing agent, lime and silicon. The second-run slag is then very low in tin and may be thrown away. Unfortunately, for slags high in FeO this method would be too expensive as much silicon would be required and much tin lost with the increased amount of ferro-silicon produced.

This consideration necessitates the re-treatment of the first-run slag in two stages. During the first stage, the first-run slag is smelted in a reverberatory or a blast furnace to remove as much tin from it as possible, with the addition of coal and lime. The limit of tin recovery depends on the iron content of the slag, decreasing with increasing iron. The metallic tin produced in the first smelting of the slag generally contains a considerable amount of the tin-iron alloy, known as "hard head". The amount of hard head produced should be limited to what is required for the return to the primary smelting to reduce the cassiterite. This amount is calculated on the basis of the requirements of the procedure chosen.

The residual tin in the slag usually runs 2.5 to 5 per cent. It can be removed by fuming the slag in reverberatory, blast or slag-fuming furnaces. In all cases, the underlying reaction is as follows:



When the slag is re-treated in reverberatory or blast furnaces, some pyrite is added to the charge, while in the case of high-iron slags an addition of gypsum is made which is reduced to CaS and reacts with the iron in the slag to form FeS. The latter reacts with tin as follows:



Slag-fuming uses granulated slag to which are added 8 to 10 per cent coal and 10 per cent gypsum. After 6 hours' smelting at 1300 to 1450°C, the tin content of the slag is brought down from 1 to 0.3 per cent. Very little hard head is produced together with some dust which carries 35 to 45 per cent Sn.

Blast furnaces may only be employed to fume the second-run slag low in iron, or too much hard head will be produced.

The second-run slag may also be fumed in molten condition when it is blown with air carrying either pulverised coal and finely divided pyrite or fuel oil and finely divided sulphur.

The fuming of tin sulphides from tin slags is similar to the fuming of lead and zinc from lead-smelting slags and uses similar furnaces (see Sec. 68). The formation of hard head and matte is prevented by blowing the charge alternatively with a reducing and an oxidising blast, the latter being a mixture of fuel and excess air. This method re-treats both the slag and the ferro-silicon, and the clean slag carries but 0.1 per cent Sn at the most. Fuming furnaces provide the cheapest method of re-treating high-iron slags and make it possible to remove very much tin and rare metals.

77. Tin Refining by Heat Treatment

The reduced tin obtained in the smelting of tin concentrates or slag must be refined before it is ready for the market. A comparison of Table 35 presenting the requirements of a relevant U.S.S.R. State Standard for the purity of commercial tin, and Table 36 showing the analyses of reduced tin gives an idea of how much refining is necessary.

Two methods of tin refining have been used. In the first of the two methods the tin is refined by heat treatment, and in the second by electrolytic treatment.

Table 35

Tin Analysis to U.S.S.R. State Standard

Grade	Min. tin, per cent	Max. impurities, per cent							
		As	Fe	Cu	Pb	Bi	Sb	S	total
O1	99.90	0.015	0.009	0.01	0.04	0.01	0.015	0.01	0.10
O2	99.56	0.020	0.02	0.03	0.25	0.05	0.05	0.02	0.44
O3	98.35	0.10	0.05	0.10	1.0	0.06	0.30	0.04	1.65
O4	96.25	0.10	0.05	0.15	3.0	0.10	0.30	0.05	3.75

Table 36

Analysis of Pig Tin
(per cent)

Concentrate	Sn	Impurities					
		As	Fe	Cu	Pb	Bi	Sb
Rich (over 60 per cent Sn)	98.5	0.1	1.0	0.2	0.1	—	0.1
Lean (over 40 per cent Sn)	97	0.4	1.3	0.4	0.5	0.1	0.3

A flow-sheet of the heat-treatment method is given in Fig. 124. Although the method is fairly complicated, it is employed more often than electrolytic treatment in which the tin has to be left in the slowly dissolving anodes for a long time. Lack of knowledge of the electrolytic process also limits its use.

The removal of iron and copper is based on the reduction in their solubility when the molten tin is allowed to cool (Fig. 125). Practically, it is accomplished by liquating or sweating tin bars, pigs or slabs at a temperature just above the melting point of tin. As the tin cools, crystals of FeSn_2 which are more refractory than tin separate out. They form a porous dross which entraps much molten tin. Some of the crystals of FeSn_2 remain in the clean tin, and its purity proves lower than may be expected theoretically.

Liquation or sweating may be improved by adding some pulverised coal to the tin. Floating to the surface of the molten metal, the coal will carry crystals of FeSn_2 along and outside. At the same time, some of the copper, arsenic and antimony will be eliminated, which also form the intermetallic compounds Cu_3Sn (melting point, 675°), Sn_3As_2 (596°), FeAs (1030°), Fe_2As (919°), Cu_3As (825°), Cu_2Sb (585°), FeSb_2 (726°C), etc. Liquation with the addition of coal is conducted at 550°C , leaving only about 0.2 per cent Fe in the clean tin, and 25 per cent Fe in the dry dross.

The remaining iron is then eliminated together with the copper for which purpose sulphur is stirred into the metal as in lead drossing.

When reduced lead contains less than 1.5 per cent Fe, liquation with coal may be dispensed with. Instead, up to 5 kg of sulphur per ton is stirred into the molten tin at 320 to 350°C , the exothermal reactions that follow raising the temperature of the metal to 400 – 500°C . The dross rising to the surface contains 5 to 10 per cent Cu.

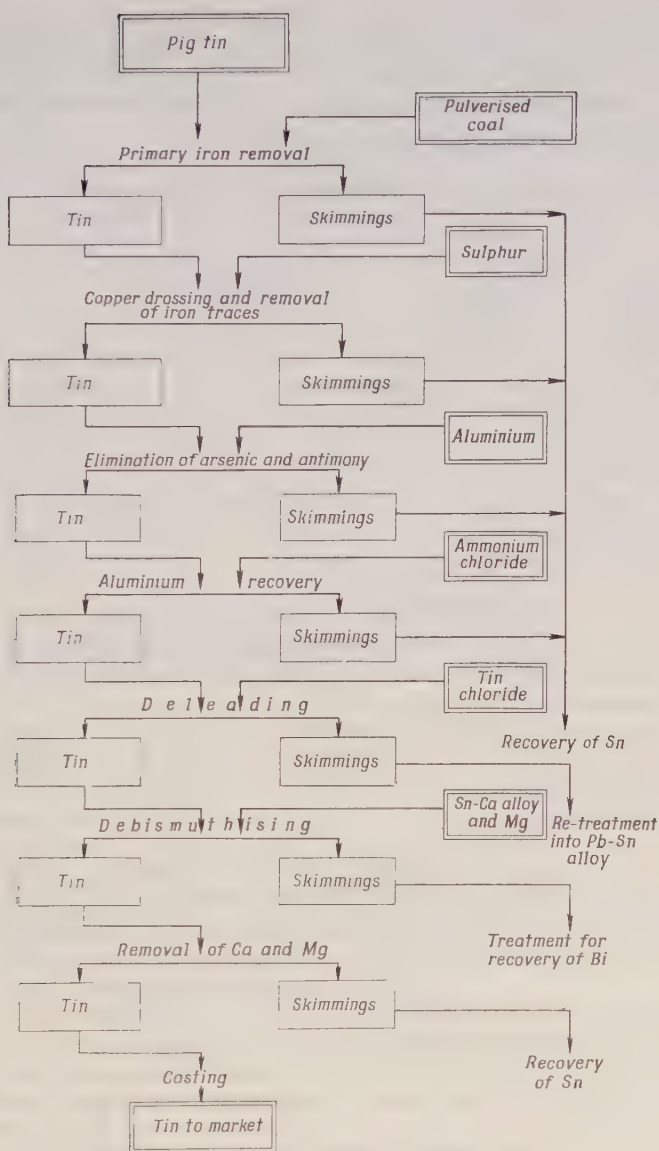


Fig. 124. Flow-sheet for tin refining by heat treatment

The elimination of arsenic and antimony is based on the formation of AlAs and AlSb insoluble in tin and melting at 1720°C and 1070°C, respectively. The required aluminium is stirred into the kettle at about 550°C in the proportion of 1 kg per ton of tin. Before

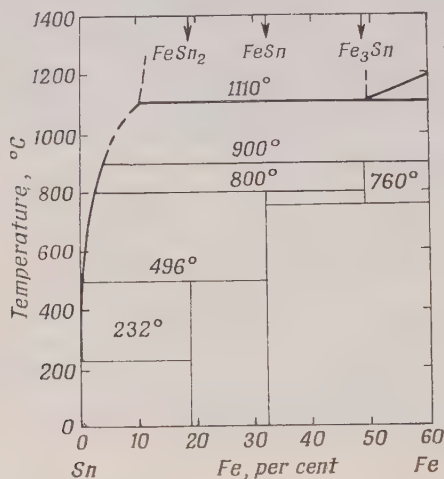
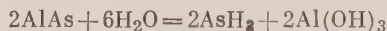


Fig. 125. Constitution diagram of the system Fe-Sn

the dross is removed, some ammonium chloride is added causing the droplets of tin entrained by the dross to coalesce and separate out of the dross.

The arsenic-antimony skimmings carry up to 10 per cent As + Sb and 55 to 75 per cent Al, and they should be immediately re-treated for their recovery, as the skimmings react with the moisture of the air to produce toxic hydrogen arsenide and antimonide:



Surplus aluminium is removed by stirring into the molten tin at 300°C first ammonium chloride and then pulverised coal. The aluminium is oxidised:

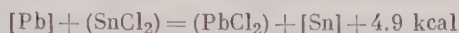


The coal facilitates the separation of the AlCl₃ from the tin.

The iron and copper drosses, as well as the antimony and arsenic skimmings produced in tin refining are smelted together in reverberatory or electric furnaces. The iron is slagged off, while the arsenic and antimony pass off with the flue gases. When sufficiently high in copper, the copper dross may be re-treated separately for the production of blue stone.

The removal of lead from tin is based on their difference in affinity for chlorine. In this method, tin chloride is stirred into molten

tin at 240 to 260°C, and the former reacts with the lead as follows:



The lead chloride and tin chloride dissolve in each other, and their alloy floats to the surface, solidifies and is removed as a solid crust.

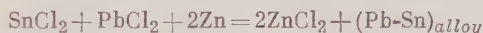
The equilibrium for lead chloridising may be written as follows:

$$K = \frac{a_{[\text{Pb}]} \cdot a_{(\text{SnCl}_2)}}{a_{(\text{PbCl}_2)}}; \quad a_{[\text{Pb}]} = K \frac{a_{(\text{PbCl}_2)}}{a_{(\text{SnCl}_2)}}$$

whence it follows that the residual lead content decreases with increasing SnCl_2 in their alloy. Accordingly, it pays to use the chloride dross for relining the more impure tin.

Tin chloride is stirred into the charge at 240 to 245°C, and then the molten tin is heated to 260°C when the chloride dross is thoroughly skimmed off. An addition of soda ash helps cleaning.

The chloride dross usually carrying up to 15 per cent Pb is resmelted on the surface of molten zinc; the following reaction takes place:



The tin-lead alloy goes to make babbitts, and the zinc chloride is a salable product by itself. It takes 40 to 70 kg of crystalline tin chloride prepared by dissolving tin in hydrochloric acid to remove 1 kg of lead.

Bismuth is eliminated from tin much as it is in lead refining, i.e., by adding calcium and magnesium which form Bi_2Mg_5 , Bi_2Ca_3 and Bi_3Ca , poorly soluble in tin. To this end, the molten tin is raised to 380°C, finely divided magnesium is stirred in, cooling to 270°C follows, and an alloy of tin and 3.5 per cent Ca is added. The bismuth dross rising to the surface of the bath carries up to 2 per cent Bi; some of it is returned to the process, and the bulk is re-treated for the recovery of bismuth.

The above method reduces the bismuth content of the tin only to 0.05 per cent, which corresponds to Grade O2. The excess calcium and magnesium are removed by adding NH_4Cl at 280 to 300°C, when the following reaction takes place:



All tin-refining operations are conducted successively in one and the same kettle, taking up as much as 40 hours. The yield of market tin amounts to 87 or 88 per cent of the weight of the pig tin.

78. Electrolytic Refining of Tin

In the standard potential series, tin is more electronegative than antimony, arsenic, bismuth and copper. Accordingly, the electrolyte used for its refining must not dissolve these metal impurities. The most common solutions based on sulphuric and hydrochloric acid do not meet this requirement. Furthermore, the cathode deposit of tin obtained from such solutions is loose and may bring about a short circuit between the anode and the cathode.

At one time use was made of hydrofluosilicic electrolyte which contained H_2SiF_6 and Sn_2SiF_6 , for it met the above requirement and did not dissolve antimony, bismuth or copper. The dissolution could be prevented by adding sulphuric acid and the formation of a loose deposit by the introduction of cresylic acid and glue. Unfortunately, this electrolyte was found to be toxic and also to passivate the anode owing to the formation of a film of lead sulphate and silica gel. So, it gave way to sulphur-organic acids obtained by the reaction of strong sulphuric acid on benzene, phenol, cresol and other aromatic compounds. An approximate composition of such an electrolyte (in per cent) follows:

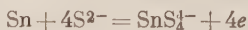
Cresolphenolsulphonic acid	4.0
Sulphuric acid	8.0
Tin	3.0

With this bath, a current efficiency of 85 per cent at a voltage of 0.3 to 0.35 V could be attained at a current density of 85 to 108 A/sq m and a temperature of 35°C. Reduced tin containing 90 to 99 per cent Sn could be treated to Grade O1, leaving a slime of the following composition:

Pb	Cu	As	Sb	Bi	Sn
20	5	3	5	20	30

The electrolyte had to be changed at fairly frequent intervals owing to the impurities accumulating in it. The anodes, too, were passivated by the depositing basic salts of tin. All in all, sulphur-organic acids did not find any appreciable use in the industry, their high cost also adding to this outcome.

Still another electrolyte containing sodium thiostannate (Na_4SnS_4) and sodium sulphide was suggested way back in the past century. In this electrolyte the tin anodes dissolve as follows:



At the cathode, the same reaction is reversed, producing a dense tin deposit. The impurities Fe, Cu, Pb and Bi appear in the slime as insoluble sulphides. The current efficiency with this electrolyte is

95-98 per cent, and the energy consumption 150 to 200 kWh per ton of lead.

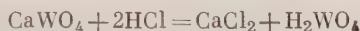
This electrolyte is furthermore free from the passivating effect on the anodes and from the rapid accumulation of impurities. It should be noted, however, that it requires a hot bath (70 to 90°C) and low current densities (50 to 100 A/sq m). Among its demerits are the hot electrolyte, difficulties in purifying it, and in re-treating the slimes.

79. Extraction of Other Metals from Tin Ores

The main metal found associated with tin in tin ores is tungsten as tungstate, or wolframite, of iron and manganese (Fe, Mn)WO₄, and calcium tungstate, or sheelite CaWO₄.

Wolframite is magnetic and can be extracted by magnetic separation.

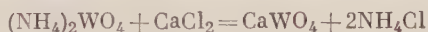
Sheelite is separated by flotation. Fine slimes of sheelite and cassiterite, however, are extremely difficult to separate. Therefore, its flotation is followed by the reaction with hydrochloric acid which converts the sheelite to insoluble tungstic acid:



After the calcium chloride and excess HCl are washed off, the residue is treated with ammonia, and the tungstic acid is converted to soluble ammonium tungstate:



The solution of (NH₄)₂WO₄ is treated with CaCl₂ to precipitate calcium tungstate—an excellent man-made sheelite:



The extraction of the considerable contents of lead, zinc and copper from lode tin ores has not yet been sufficiently investigated.

The same applies to the extraction of rare-earth metals, titanium, bismuth, indium and scandium. Rare-earth metals and titanium are present in some tin minerals and may be separated by, say, electrostatic and magnetic separation. Bismuth, indium and scandium usually pass into tin concentrates as a result of ore beneficiation. In the subsequent leaching of tin concentrates with hydrochloric acid, the bulk of the bismuth passes into solution and can be precipitated by hydrolysis as the chloroxide BiOCl. The bismuth remaining in the tin concentrate after leaching goes into pig tin and then, during refining, into bismuth skimmings. Indium is distributed between the flue dust and pig tin. Scandium accumulates in tin-smelting slags.

Chapter X

THE METALLURGY OF ZINC

80. General

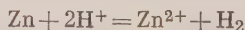
Zinc is a coarse-grained metal which is brittle and anisotropic at normal temperature. At 100 to 150°C it can be easily rolled into sheets and drawn into wire.

Metallic zinc has a hexagonal close-packed crystal structure and a density of 7.13 to 7.14 g/cu cm at 20°C. It melts at 419.6°C and boils at 906°C. In all compounds zinc is bivalent.

Pure zinc is highly resistant to attack by dry air at below 200°C, due to the film of basic carbonates formed on its surface which hampers the passage of oxygen to the unoxidised metal. At a higher temperature, the rate of attack increases rapidly, especially above its melting point.

The electrode potential of zinc is -0.76 V, but at ordinary temperature zinc does not decompose water owing to the high hydrogen overvoltage on it. Near its melting point zinc is oxidised by water vapour with the evolution of hydrogen.

Zinc is amphoteric, producing two-charge ions when dissolved in acids:



In hot caustic solution it dissolves forming anions:



The resultant compounds are called zincates; zincates of alkaline metals readily dissolve in caustic solutions.

At elevated temperatures zinc oxide (ZnO) acts as a weak base capable of producing salts with ferric oxides (zinc ferrites), with silica (zinc silicates) and with alumina (zinc aluminates).

Zinc as metal is used for many purposes. The major use (45 per cent of all zinc) is in galvanising, i.e., coating of iron and steel as a protection against corrosion. The second most important use of zinc is in the die-casting of parts for the automotive, radio-engineering and other industries (with small additions of aluminium, copper and magnesium). It also finds use in photoengraving and printing plates. Other important uses are in brass and bronze alloys, roofing sheets, rolled and extruded products, and in the production of zinc salts.

Zinc compounds are widely employed in many applications. Zinc oxide and zinc sulphide (lithopone), both white powders, go to make zinc white. Large quantities of zinc oxide are consumed in the manufacture of viscose rayons, glazes, enamels, glass, grinding materials, and oil-cloth. Specially treated zinc sulphide is added to phosphorus used in fluorescent lighting fixtures and television.

Zinc chloride finds use as a wood-preservative protecting timber against rot.

Zinc sulphate is used in the manufacture of the pigment lithopone, and as a flotation reagent.

The properties of zinc vary with its purity. For the alloys employed in die-casting, the content of impurities in the zinc must not exceed 0.01 per cent, the most detrimental impurity being lead which increases corrosion. In rolling, on the other hand, lead is a useful addition.

81. Zinc Ores

Zinc is found in nature as a few minerals. The principal among them is zinc sulphide, ZnS , known as sphalerite or zinc blende, and its variety marmatite which is an isomorphic mixture of zinc and iron sulphides $(\text{Zn}, \text{Fe})\text{S}$. Next in importance are zinc carbonate ZnCO_3 known as smithsonite, and zinc silicate, $\text{Zn}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$, called hemimorphite or calamine. The other minerals occur seldom and are of no commercial value.

Zinc ores generally range from 2.0 to 7.5 per cent zinc metal. Complex lead-zinc ores are covered elsewhere in the book. In this chapter, the discussion will be limited to the concentrates obtained from the differential concentration of complex ores.

Zinc concentrates assay 47 to 60 per cent Zn, 1.5 to 2.5 per cent Pb, up to 3.5 per cent Cu, 3 to 10 per cent Fe, about 0.2 per cent Cd, and 29 to 33 per cent S, as well as minor quantities of thallium, indium, gallium, germanium, selenium, and tellurium.

An approximate mineralogical composition of a zinc concentrate assaying 47.66 per cent Zn follows (in per cent):

Sphalerite	70.3
Galenite	5.2
Chalcopyrite	3.1
Pyrite and other iron sulphides	11.3
Silicates and carbonates	10.1

A zinc concentrate is a powdered material with 50 to 95 per cent particles less than 0.07 mm on side, the grains measuring more than 0.6 mm accounting for not over 0.1 to 0.3 per cent.

In the case of oxide ores, a concentrate will usually consist of mainly smithsonite and calamine.

82. General Principles of Zinc Extraction

The metallurgy of zinc is divided into two fields: pyrometallurgy and hydrometallurgy. The former is mainly presented by the distillation processes, and the latter by the electrolytic processes.

The distillation processes appeared well before the electrolytic methods. Outside the Soviet Union zinc distillation still dominates the industry, accounting for over half the zinc produced. In the

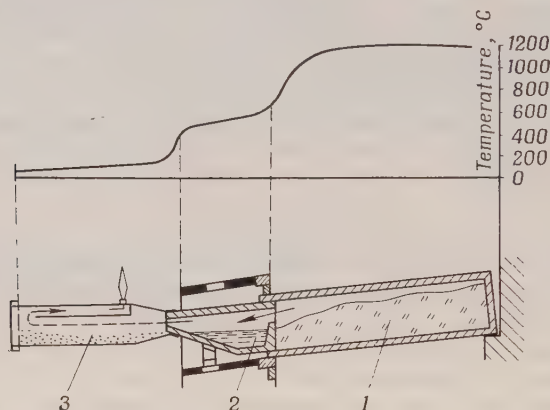


Fig. 126. Diagram of the horizontal retort process:
1—retort; 2—condenser; 3—prolong

Soviet Union, preference has always been given to the electrolytic processes. Here is a general outline of both groups.

Zinc distillation. A mixture of roasted zinc concentrate and anthracite screenings or coke breeze is charged into a grog retort (Fig. 126) which is then placed in a furnace heated to 1400°C.

In the retort the zinc is reduced according to the reaction:



The nose of the retort opens into a condenser of fireclay. In the condenser, the retort gas cools in contact with its walls, the droplets run down the sides, and fall from the top, collecting in the pool at the bottom. The liquid zinc is drawn from the pool as it accumulates there.

The zinc vapour that escapes from the condenser is precipitated in the prolong, a sheet-iron extension to the condenser, as a dust.

The other oxides present in the charge, such as those of cadmium, lead and copper, may also be reduced in the retort. Of these metals, however, only cadmium and lead can vaporise to an appreciable extent.

The material left in the retort is called the retort residue.

The horizontal retort process outlined above is simple but of low capacity, producing metallic zinc contaminated with cadmium and lead. A diagram of the horizontal retort process is shown in Fig. 127.

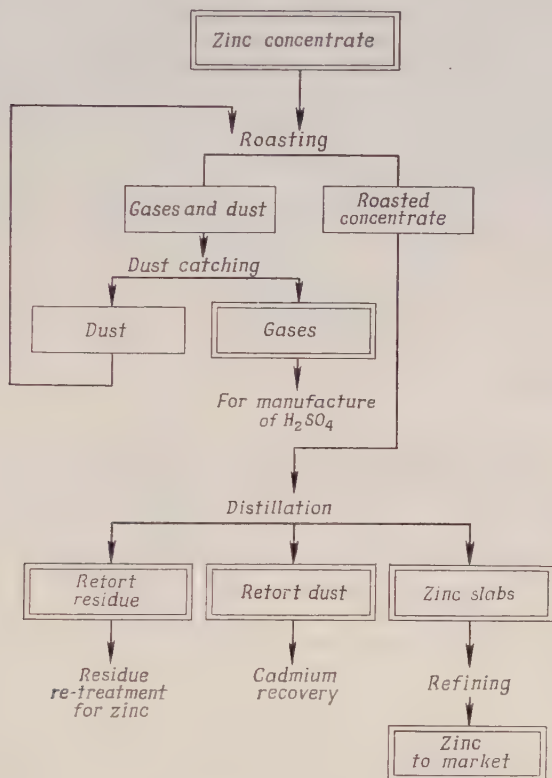


Fig. 127. Flow-sheet for zinc pyrometallurgy

Horizontal retorts are made from 300 to 370 mm in diameter, with walls 30 to 50 mm thick; thicker walls would hamper heat transfer inside the charge and slow down the rate of distillation. The length does not exceed 1700 to 1900 mm, as at a temperature of 1400°C the retort will fail under the bending load.

A single charge of such a retort weighs 80 to 90 kg, containing up to 30 kg metallic zinc. With a distillation cycle of 24 hours and a liquid zinc yield of 80 to 83 per cent of the charge weight, a single retort can produce 25 kg of zinc a day at the most. So, an average zinc smeltery will have several thousand retorts in operation simulta-

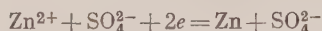
neously. The retorts are handled manually; the attempts to mechanise their handling have so far failed. Therefore, the retort process involves arduous manual labour.

Far better results are obtained with continuous vertical retorts and blast furnaces.

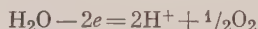
The *hydrometallurgy of zinc* dates back to 1915. It consists in leaching roasted zinc concentrate with sulphuric acid. The gangue is mainly insoluble. The zinc sulphate solution thus obtained is purified and electrolysed. Metallic zinc is deposited at the cathodes, while oxygen is released at the anodes, and the solution accumulates sulphuric acid which may be re-used to leach roasted concentrate (hence its name, "return acid").

The reactions taking place in the electrolytic zinc process may be presented as follows:

At the cathode:



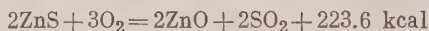
At the anode:



A flow-sheet of the electrolytic zinc process is shown in Fig. 128.

83. Roasting of Zinc Concentrates

The main purpose of roasting zinc concentrates is to convert the zinc sulphide to zinc oxide and to expel the sulphur dioxide gas. Accordingly, the principal reaction of concentrate roasting is:



The ignition point of zinc sulphide depends on its mineralogical composition and grain size. Marmatite ignites easier than sphalerite. Furthermore, when heated to 200-300°C, grains of marmatite crack up, thereby facilitating their ignition. For practical purposes it may be assumed that the zinc sulphide concentrate ignites at anywhere between 550°C and 600°C. The rate of combustion increases with increasing temperature and decreases as more sulphur is burned out, for the reason that the oxide film forming on the surface of each grain shuts out oxygen.

The heat balance of the roasting operation is made up of the heat input from the combustion of the sulphides and the heat losses to the surroundings. As the rate of combustion is reduced, heat input per unit time is reduced too and at a certain moment of time it becomes equal to the heat losses. It is at this moment that the spontaneous burning of the sulphides ceases. Too high a temperature of roasting may cause the particles to sinter or fuse, which fact would hamper the inflow of air to the sulphides and the rate of combustion of the sulphur would drop rapidly.

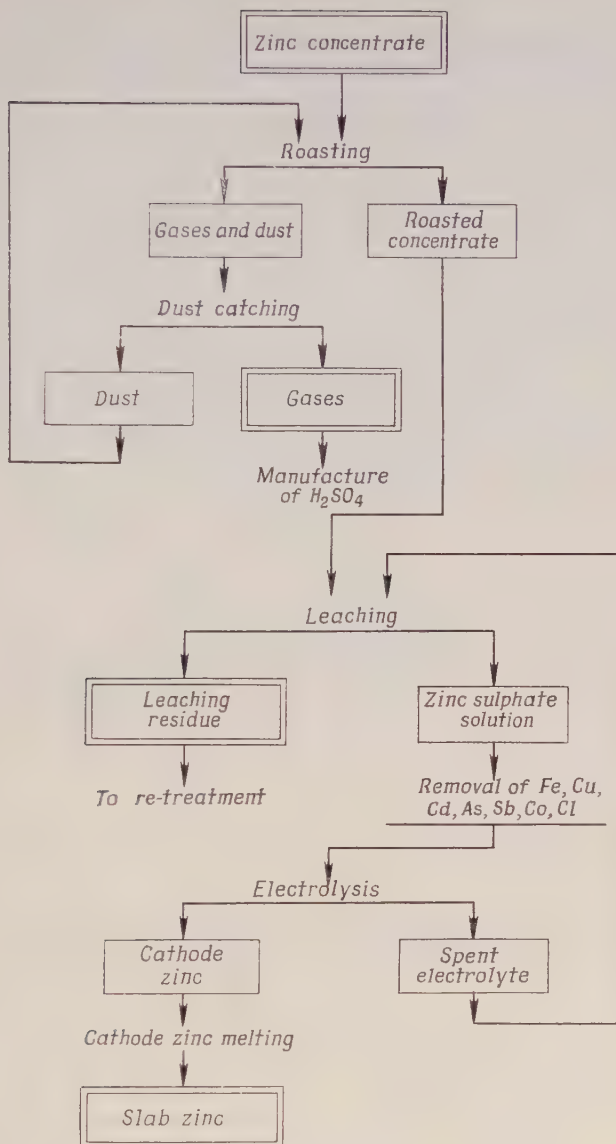


Fig. 128. Simplified flow-sheet for zinc hydrometallurgy

In roasting, some of the zinc sulphide is oxidised to zinc sulphate, which may be expressed by the following, equations:



The impurities contained in the zinc concentrate are oxidised in roasting to form Fe_2O_3 , CuO , CdO , Sb_2O_3 , and As_2O_3 . The oxides of arsenic and antimony partly pass off as fumes, and are partly oxidised to higher and less volatile oxides.

The acid oxides SO_3 , As_2O_5 , Sb_2O_5 , Fe_2O_3 , SiO_2 , etc., react with the basic oxides and carbonates, i.e., CdO , FeO , CuO , PbO , CaCO_3 and MgCO_3 to form respective zinc sulphates, arsenates, antimonates, ferrites and silicates. Not all of the many possible reactions here reach completion owing to the fact that either the reacting materials are not present in stoichiometric proportions, or contact between them is upset, or the rate of interaction is too low. The most detrimental secondary reactions in roasting are those producing ferrites of zinc and cadmium and silicates of lead and zinc. The latter, reacting with the sulphuric acid in the subsequent leaching, form colloidal silicic acid which hampers filtration and settling. Zinc ferrite, on its part, reacts with sulphuric acid but slowly, and the zinc fixed in it does not practically pass into solution. At low temperatures, the rate of zinc ferrite formation is insignificant, but it rapidly increases at above 650°C . The largest quantity of zinc ferrite is produced in roasting zinc concentrates containing marmatite for the reason that in marmatite sulphides of zinc and iron make up an isomorphic mixture.

Until the 1930s, zinc concentrates had been predominantly roasted in mechanically-rabblled multiple-hearth roasters. Since then much ground in the roasting field has been captured by the suspension technique. The suspension roasting process has its origin in the observations over the behaviour of the concentrate falling from hearth to hearth in a conventional roaster. In falling down, the concentrate particles come in contact with oxygen-bearing gases and burn quickly. The rate of combustion "in the midair" is greater than the rate of heat transfer to the surroundings, and the temperature of combustion rises appreciably. As a result, dead-roasting becomes possible without auxiliary heating. Furthermore, a smaller excess of air is required for suspension combustion as the oxygen is utilised to a fuller extent, and the SO_2 content of the roasting gases increases.

The furnace used in the suspension roasting process (Fig. 129) is in fact a remodelled multiple-hearth mechanically-rabblled roaster with some of its middle hearths removed to form a fairly large com-

bustion chamber. It has three collecting and sulphatising hearths and two drying hearths placed under a roof.

The wet concentrate is fed onto the enclosed drying hearth; the rabble arms move the material to the centre hole through which the dried product falls onto the next drying hearth, below. On

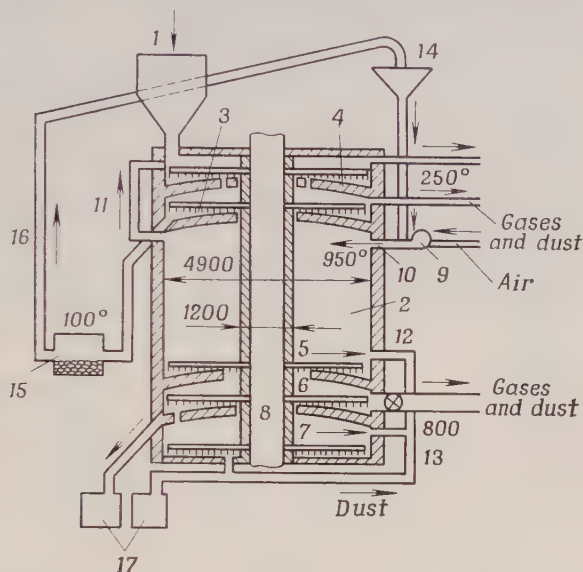


Fig. 129. Scheme for the suspension roasting process:

1—green concentrate bin; 2—combustion chamber; 3, 4—drying hearths; 5, 6, 7—bottom sulphatisation hearths; 8—shaft; 9—fan; 10—concentrate burner; 11, 12, 13—gas-recirculation flues; 14—dry concentrate bin; 15—ball mill; 16—elevator; 17—calcine
hoppers

the periphery of the next drying hearth the concentrate is discharged into a ball mill in order to break up the agglomerations and to grind the material further if necessary.

The ground material is collected in a feed bin from which it is fed at a controlled rate into the combustion air stream. The air stream carries the dried concentrate, along with the drying gases, to a burner placed tangentially on the side of the combustion chamber. The particles blown in by the burner follow a spiral path so that they remain suspended in the air for a longer time. The sulphur elimination is about 95 per cent complete by the time the particles settle on the hearth, and the temperature in the combustion chamber reaches 930 to 950°C.

Two hearths at the base of the furnace eliminate what sulphur may remain in the product, and the lowermost hearth performs sulphur-

tisation. Some of the hot-chamber gases are recirculated, which fact increases their SO_2 content, the heat is better utilised, and less dust is carried off with the gas stream.

From the combustion chamber the gases heated to about 900°C follow three paths: a small proportion is recirculated to the upper hearths for drying the wet concentrate; another part is utilised on the sulphatising hearth; and the bulk of the gases is passed through a gas-handling system to remove dust.

The temperature at the drying hearths is 120 to 260°C , at the lowermost sulphatising hearth 500°C and of the gases leaving the furnace 800°C . The daily capacity of a furnace is 110 to 120 tons of wet concentrate, but it may be raised to 200 tons by using an oxygen-enriched blast. The final product usually assays 0.3 per cent sulphide sulphur and up to 3 per cent sulphate sulphur. The gases carry off with them up to 40 per cent of the total calcine.

Among the drawbacks of the suspension roasting process are the complexity of concentrate preparation and the necessity to additionally roast the product on the bottom hearths as the sulphide particles do not remain suspended for a sufficient time.

Much better results are obtained with fluidisation or fluid-bed roasting processes. These processes which have come into prominence during the last decade are being widely employed not only in the zinc industry but also for roasting copper, antimony, molybdenum, pyrite and other concentrates. The fluid-bed technique is employed to roast lead oxide ores by fuming the lead and to calcine limestone, dolomite and many other materials fed as a mixture with fuel.

The bed of powdered material is fluidised by blowing air through a dispersion plate having holes uniformly spaced over its area. Rising through the bed of material the air brings the charge into a state resembling the boiling of a liquid. In effect, the material resembles a fluid as it can flow from a higher to a lower level. In the fluidised bed the surface of each particle is constantly blown over with air, and so the roasting proceeds at a very high rate and to completion.

Furnaces or reactors for the fluidised-bed roasting process are built either round or rectangular in plan. Fig. 130 shows a circular furnace. The walls and roof are made of firebrick, and the hearth is in heat-resistant concrete. The incoming air is uniformly distributed by the dispersion plate fitted with nozzles shown in Fig. 131. The feed is introduced from one side of the reactor and the calcine discharges through an overflow on the opposite side. The stay of the material in the fluidised bed, i.e., the roasting time, depends on the rate of feed and air flow.

The quantity of air blown into the reactor has a decisive effect on the condition of the bed. With an excess of air, the particles

pass into suspension and are carried out of the reactor. With too little air blown in, fluidisation is upset, and the bed settles down, only filtering the air.

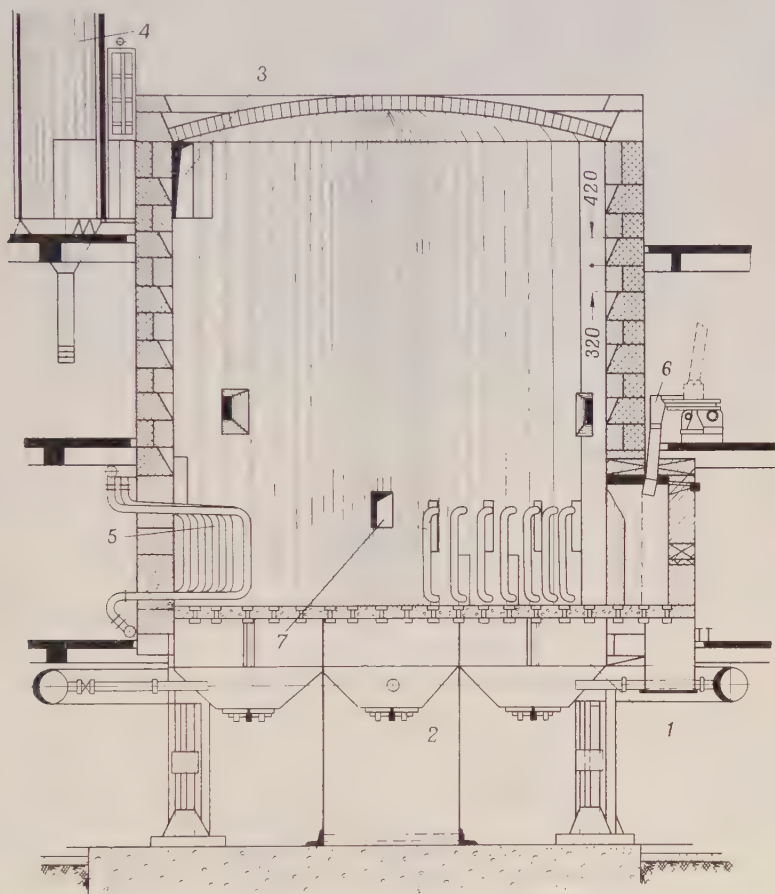


Fig. 130. Fluidised-bed roaster:

1—hearth and nozzles; 2—wind-boxes; 3—gas flue; 4—cyclone; 5—water coils; 6—charging chute; 7—calcine discharge hole

No auxiliary heating is required for roasting sulphide concentrates by the fluidisation process, for the quantity of heat generated by the rapid combustion of the sulphides is enough to maintain the requisite temperature in the reactor. The temperature can be controlled

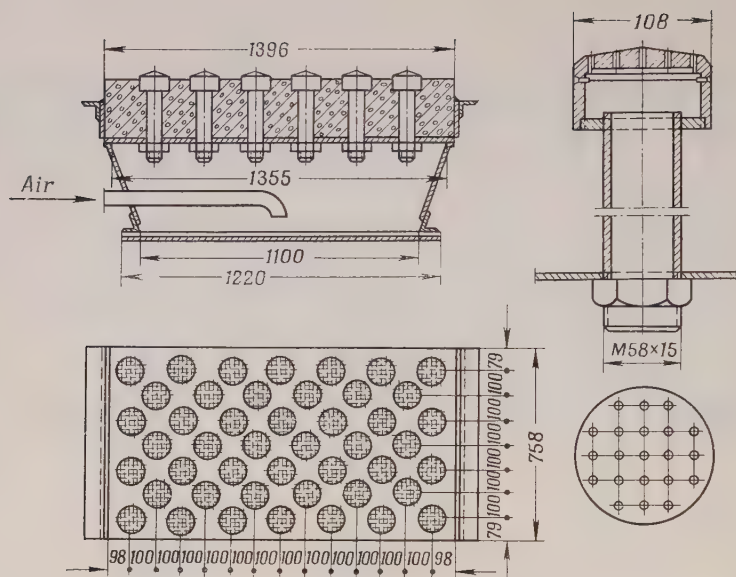


Fig. 131. Hearth of a fluidised-bed roaster

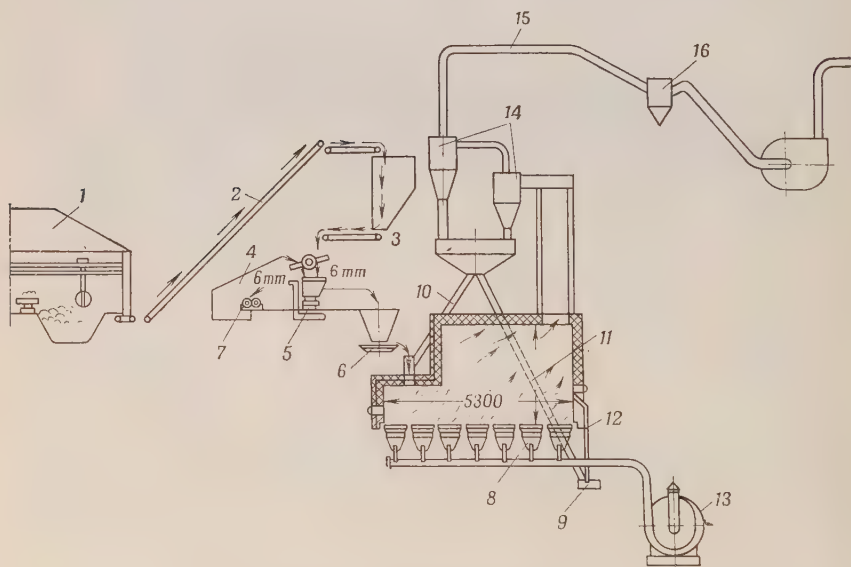


Fig. 132. Flow-sheet for fluidised-bed roasting:

1—stockyard; 2—conveyers; 3—screen; 4—elevator; 5—scale; 6—feeder; 7—rolls; 8—hearth chambers; 9—launder; 10—dust flue; 11—furnace; 12—calcine discharge hole; 13—blower; 14—cyclones; 15—gas flue; 16—electrostatic precipitators

by varying the rate of feed and also by means of water coolers built into the reactor at the level of the fluidised bed.

Some of the material inevitably goes into suspension and is carried off with the gas stream. The coarse dust carry-over is precipitated in two stages in cyclones. The fine dust is caught in electrostatic precipitators installed past the cyclones. The fine dust carry-over amounts to 3 to 6 per cent of the charge. It is either added to the calcine or re-treated separately. Fig. 132 shows a flow-sheet for fluidised-bed roasting.

The materials roasted by a fluidised-bed process may have a high moisture content or even fed as a slurry.

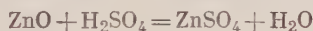
The daily capacity of fluidised-bed reactors treating zinc concentrates is three times that of multiple-hearth roasters (by volume). Owing to a moderate excess of air, the SO_2 content of the hot gases rises to 12 per cent, or doubles itself.

A reactor with a hearth area of 33 sq m can treat 150 to 160 tons of concentrate per 24 hours.

Fluidised-bed reactors lend themselves readily to automation. At many smelteries the temperature of the fluidised bed is controlled to within $\pm 20^\circ\text{C}$ by automatically varying the rate of feed and air blow.

84. Leaching of Roasted Zinc Concentrates

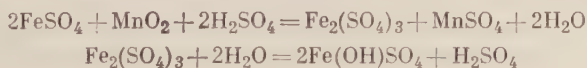
The primary purpose of leaching a zinc concentrate is to dissolve the zinc oxide:



Being a simple process in itself, it is complicated, however, by the simultaneous dissolving of unwanted elements and compounds which have an adverse effect on the electrolysis and recovery of zinc. For this reason, a two-prong approach has to be taken to the leaching operation: firstly, to minimise the amount of impurities passing into solution; secondly, to purify the solution.

Many of the impurities can be reduced in amount or eliminated by neutralising the zinc sulphate solution with zinc oxide, with the formation and precipitation of ferric hydroxide.

This method is commonly called "iron purification" and is usually carried out simultaneously with leaching. To this end, any ferrous iron present is first oxidised to the ferric state with manganese dioxide and by hydrolysing the ferric sulphate:



The first reaction is possible in an acid medium; therefore, the iron has to be oxidised at the beginning of the leaching operation. The second reaction is feasible only at the end of the leaching when the acid has been depleted and the solution is almost neutral.

The arsenic and antimony are removed from the solution simultaneously with the iron. Good elimination of the two impurities is obtained if the amount of iron present is 10 to 20 times that of arsenic and 20 to 40 times that of antimony. Some ferrous sulphate may be added to the solution if there is not enough soluble iron present.

The complete recovery of zinc requires an excess of sulphuric acid. On the other hand, the solution should be neutral towards the end of the leaching operation if the iron is to be withdrawn successfully. To meet these conflicting requirements, the leaching operation is carried out in two stages (double leaching). First, roasted concentrate is treated with a slightly acid solution of ZnSO_4 containing about 100 to 130 grams of zinc per litre and 1 to 5 grams of free sulphuric acid per litre. The acid present will not leach out all of the zinc—only some of it will pass into the solution which will be neutral and therefore clean of iron. This stage is called the neutral leach. The insoluble residue of the neutral stage still carries much zinc, and it is re-treated by depleted electrolyte containing about 100 grams of H_2SO_4 per litre in the second stage called the acid leach. Towards the end of the second stage, the concentration of sulphuric acid in the solution drops to 1-5 grams per litre, and it is used for neutral leaching (see the flow-sheet in Fig. 139).

The rate of leaching depends on the concentration of sulphuric acid. As it is higher in the acid than in the neutral leach, the bulk of the zinc passes into solution during the second stage. The other factors affecting the rate of leaching are temperature, the grain size of the roasted concentrate, agitation, etc.

As the temperature rises, the rate of leaching increases due to an increase in the rate of diffusion and the rate of chemical reactions between the sulphuric acid and the solid zinc compounds.

The grain size of the concentrate affects the rate of leaching above all for the reason that the coarse and fine particles differ in chemical composition. The coarse particles are mainly sintered zinc sulphides, ferrites and silicates which react with sulphuric acid but slowly. Furthermore, the zinc contained in the larger particles passes into solution more slowly than from the fines: in the coarse particles the surface of the zinc compounds may be isolated from the solution by the gangue, while in the fine particles it is exposed. As the grain size decreases, the surface area of solids per unit weight increases, and the rate of solution is directly proportional to the surface area

of the particles. This is why coarse-grained material should preferably be reground prior to leaching.

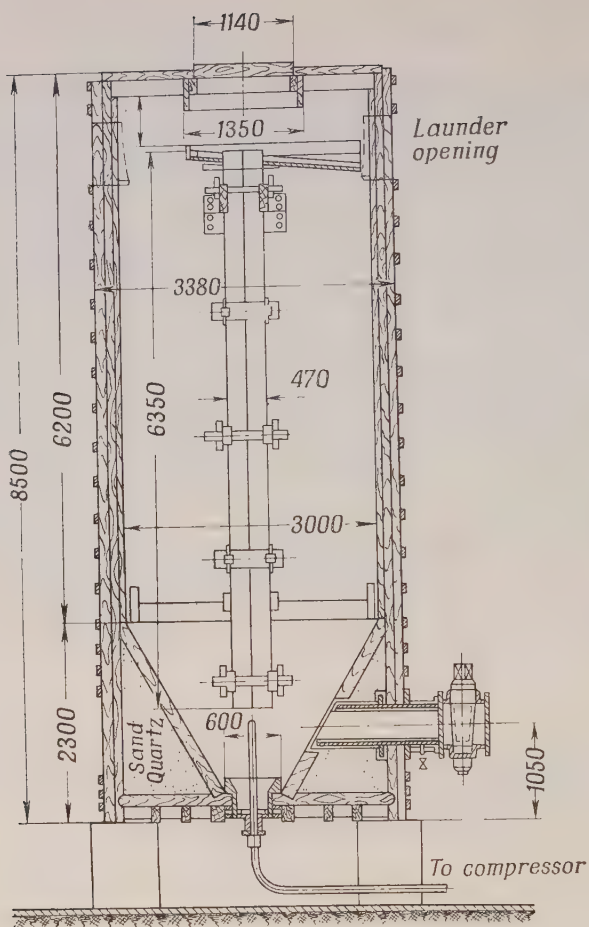
The agitation of the pulp consisting of solid particles and solvent speeds up diffusion. The solid particles should be always held in suspension for better contact between their surface and the solvent.

The equipment for leaching may be either air-operated or mechanical. In air-operated apparatus, the pulp is agitated by compressed air, and in mechanical equipment by a rotary stirrer.

An air-operated Pachuka tank (Fig. 133) is a tall cylinder with a conical bottom. The tank may be of either wood or steel plate. On the inside the steel plate is lined with either acid-proof brick or ceramic tile over a layer of hydraulic insulation as a protection against the scouring action of the sulphuric acid and salts. The tank measures 3 or 4 metres in diameter and 6 to 8 metres in height and has a capacity of up to 100 cu m. Placed centrally in the tank on supports is a wooden pipe opened at both ends. Compressed air under a pressure of about 2 atm (gauge) is supplied to its bottom end. The pulp is fed into the tank from above and overflows continuously as it fills the tank, at a level somewhat below the top end of the central pipe. Bubbling through the pulp, the air raises the level of the pulp, causing it to flow out of the pipe and into the tank. For the same reason, the pulp is continuously drawn into the pipe from below. As a result, the pulp is made to circulate in the tank all the time, and the necessary agitation of the feed is attained. The solid particles settle to the conical bottom beneath the central pipe where the circulation is most intensive, and so the particles are again driven into suspension. A drawback of air-operated tanks is that the air cools the solution.

Fig. 134 shows a mechanically agitated tank. It is made of steel plate lined with acid-proof brick. Placed centrally in the tank is a rubber-coated steel pipe with holes in the walls. The pipe encloses an impeller rotating at a speed of 40 to 100 rpm. It causes the pulp to flow downward and draws it in through the holes in the pipe. Agitation in mechanical tanks is more perfect than in air-operated apparatus; furthermore, the charge may be heated with steam passed through lead-pipe coils.

The leaching methods may be divided into batch and continuous systems. In batch leaching, a mixture of roasted concentrate and solvent is charged into a tank, agitated for a prescribed period of time, worked up with additions of calcine, and discharged. Its advantage is that elimination of impurities is more complete; it suffers, however, from some waste of time on filling and discharging the tanks. In continuous leaching the pulp passes through several leaching tanks in succession. The batch system uses mechanically agitated tanks, and the continuous system air-agitated tanks. In



Top view

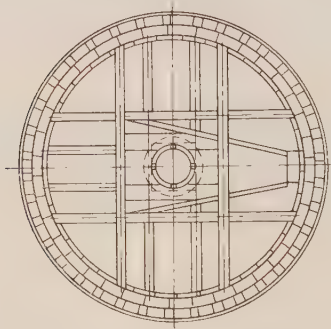


Fig. 133. Pachuka tank

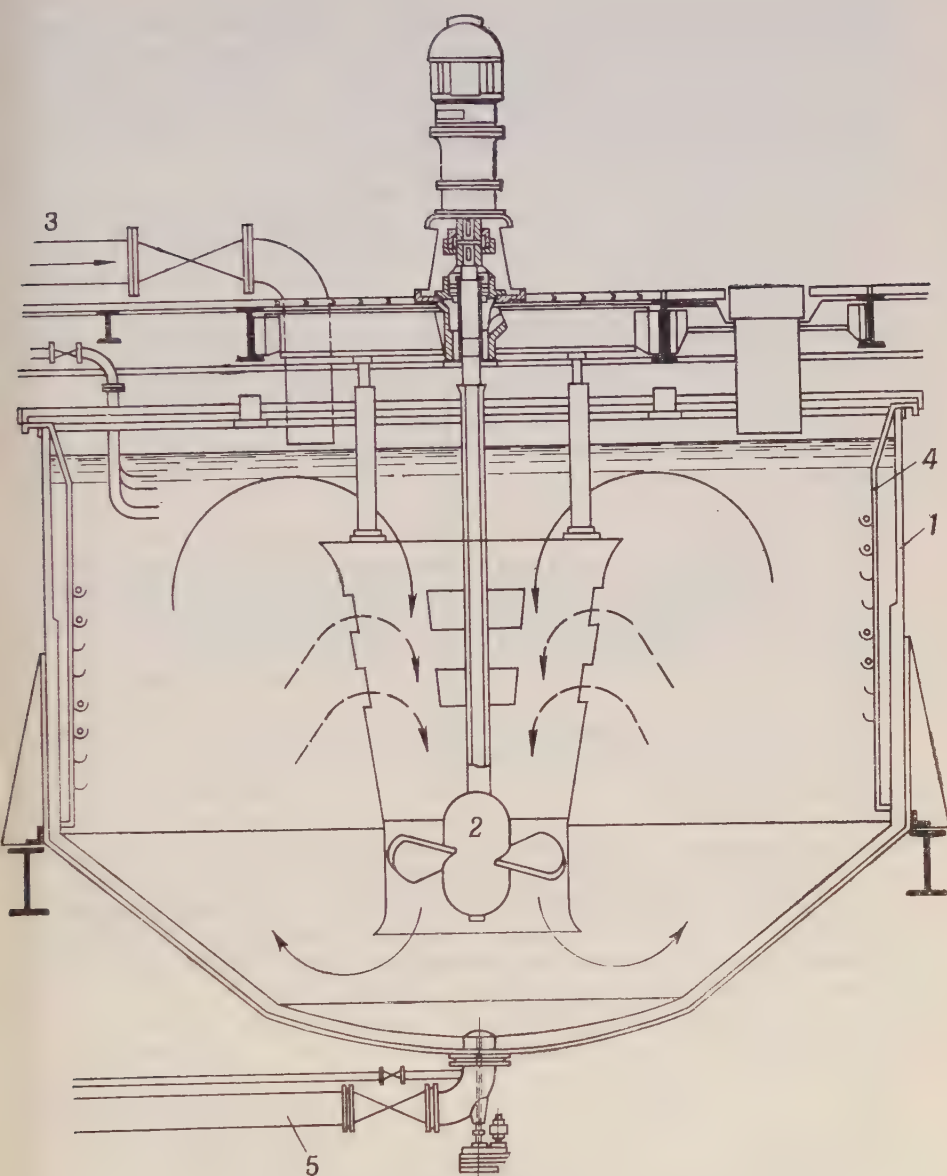


Fig. 134. Mechanically agitated tank:
 1—tank; 2—impeller; 3—feed pipe; 4—heating coil; 5—discharge hole

the case of continuous leaching, roasted concentrate is discharged from the roaster into a chute in which the solution flows. Before the resultant pulp is fed for the neutral leach it is screened through a copper netting with about 3-mm openings and then through classifiers to separate coarse particles. The residue on the copper screen is ground and returned to the roaster, and the coarse particles go to the acid leach.

At the beginning of leaching, there are about 10 to 15 parts (by weight) of solution to one part of roasted concentrate (the liquid to solid ratio is about 10-15). Three or four air-agitated tanks are connected in series, and the pulp flows continuously through them. No auxiliary heating is required, for the temperature of the pulp is upwards of 40 to 60°C owing to the heat given up by the added calcine, exothermic reactions and the heat of hydration. The dwell of the pulp in the neutral leach step is about 0.5 to 1 hour.

Towards the end of the neutral leach, the ferric sulphate in the terminal tanks is hydrolysed to form insoluble basic salts. Their precipitation assists in the removal of the compounds of arsenic and antimony.

From the terminal tank the pulp is fed into the thickeners of the neutral leach (for the design and operation of thickeners see Sec. 10). The overflow is treated for the removal of impurities, and the underflow, which is the insoluble product of the neutral leach containing 15 to 20 per cent solids and 80 to 85 per cent of the neutral solution (by weight), is partially filtered, and the residue is fed to the acid leach step.

The feed for acid leaching consists of the underflow from the neutral step and spent electrolyte which contains 40 to 60 g of zinc per litre and 90 to 160 g of H_2SO_4 per litre. In the beginning, the liquid to solid ratio of the pulp is about 10; towards the end of the leaching operation it rises to 20 owing to the dissolution of some zinc.

The temperature of the pulp is 40 to 50°C at the beginning and 50 to 60°C at the end of the acid leaching due to the exothermic reactions between zinc oxide and sulphuric acid and heat of hydration.

The acid leaching step occupies 1.5 to 2.5 hours.

The approximate composition of the acid leach (in grams per litre) follows:

Zn	Mn	Fe	Cu	As	Sb	H_2SO_4
98	3.5	0.8	2.0	0.10	0.005	5.2
100	—	1.6	0.6	0.02	0.001	3.0
120	—	1.4	3.6	—	—	4.5

The solution is allowed to settle in thickeners, the overflow is returned to the neutral leaching step, and the underflow with

a liquid-to-solid ratio of 2-2.5 is passed through filters. It does not pay to filter the whole of the pulp, as filtering is more expensive than thickening. The cake on the filters may contain up to 50 per cent (by weight) of the zinc-bearing solution. Before the cake may be thrown away, it should be re-treated with water for the recovery of the zinc, and the wash waters returned to the leaching step.

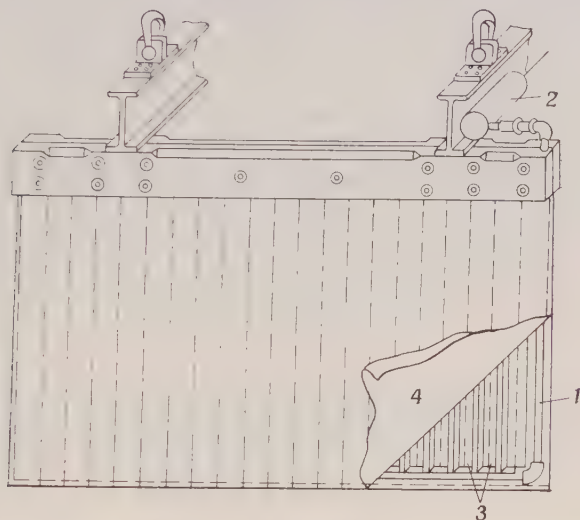


Fig. 135. Butters filter:

1—filter leave; 2—vacuum line; 3—wooden battens; 4—filtering medium

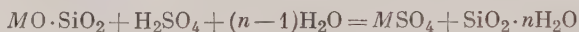
Direct washing on a filter would require much water; instead, the cake is redissolved in water, and the resultant pulp is again filtered.

The underflow from thickeners is filtered through Butters filters. Being of a non-continuous type such a filter consists of 20 to 30 filter leaves suspended from I-beams vertically in a steel or wooden tank (Fig. 135). The leaves are perforated copper pipe frames measuring 2.5 m by 3 m and supporting a filtering medium. Each filter leaf is connected to a common header. The header is connected to a vacuum-pump. The leaf assembly is lowered by an overhead travelling crane into the tank filled with the pulp. The pump builds up a vacuum, the solution passes through the filtering medium, the header and into a receiver, while a cake 30 to 40 mm thick is formed on the filtering fabric. Then the leaf assembly is taken by the crane into a water-filled tank, compressed air is forced into the header, and the cake is detached to fall into the tank. The pulp thus obtained is again filtered on drum-type or rotary disk filters. Drum and disk

filters (see Sec. 10) may only be used for refiltering, as they do not provide for adequate washing of the cake.

The efficiency of thickening and filtering varies with the composition of the zinc concentrate being treated, roasting and leaching conditions. The roasting of concentrates high in SiO_2 produces considerable quantities of zinc silicates, their formation increasing directly with SiO_2 content and roasting temperatures.

The acid leach step destroys the zinc silicates to form colloidal silicic acid:



The content of colloidal silicic acid in the leaching solution may be as high as 3 or 4 grams per litre, increasing directly with residual acidity in acid leaching. Colloidal silicic acid renders the pulp thick and slows down thickening. Depositing on the filtering medium, it bridges the pores and reduces the rate of filtrate flow. These detrimental effects of silicic acid on thickening and filtering may be controlled by roasting at lower temperatures and by conducting the acid leach at reduced pH values. The heating of the pulp prior to filtering promotes the coagulation of silicic acid.

The acid-leach residue carries about one-tenth of the zinc in the original concentrate, all lead, gold and silver. On top of it, the leaching residue contains about half the copper and part of the cadmium present in the original concentrate.

85. Purification of Neutral Zinc Sulphate Solution

Even if present in minute quantities, such impurities as copper, cobalt, iron, arsenic and antimony may appreciably reduce current efficiency in subsequent electrolysis. In the presence of some ions, such as those of antimony and cobalt, the cathode deposit will be rough and of low density; when smelted, much of the cathode zinc will be oxidised and lost.

As often as not these impurities are contained in the original concentrate and pass into the leach in some quantities. Table 37 gives an idea of the composition of unpurified neutral solutions and the requirements they should meet.

In most cases, it is essential that neutral solution be purified of its copper and cadmium prior to electrolysis. The elimination of cobalt and chlorine is sometimes of minor importance. It is conducted by withdrawing some of the electrolyte from circulation and is done in order to check their build-up.

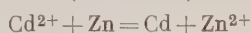
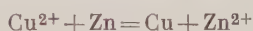
The principal reaction of copper and cadmium elimination is that of electrolytic reduction: both copper and cadmium are below

Table 37

**Approximate Composition of Unpurified Neutral Solutions
and Requirements for Their Purity**

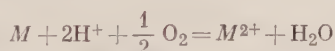
Impurity	Concentration, g/litre			
	actual (approx.)			required
	1	2	3	
Cd	0.35	0.15	0.25	0.002-0.004
Cu	3.0	0.3	0.6	0.0001-0.0005
Fe	0.03	0.03	0.002	0.02-0.03
As	—	0.03	0.001	0.0001
Sb	—	0.001	0.001	0.0001
Co	0.003	0.001	0.07	0.003-0.007

zinc in the electromotive series, and zinc replaces them:



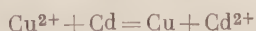
The purification is carried out with zinc dust. More zinc is added than is required theoretically to precipitate the copper and cadmium present for the reason that some of the zinc is dissolved due to the reduction of hydrogen ions. Furthermore, the deposits of copper and cadmium formed on the zinc dust particles prevent its full utilisation.

Copper and cadmium removal depends on two conflicting mechanisms—precipitation and dissolution. As more residue is precipitated, it tends to redissolve again under the action of the oxygen present in the solution:



Gradually, the rate of precipitation is reduced due to the deposit formed on the zinc dust, and that of redissolution increases. The removal may be enhanced by increasing the temperature of the solution, as this speeds up precipitation and reduces the solubility of oxygen. For better copper and cadmium removal, the purification may be carried out in two steps, with the precipitate after the first stage being passed through filters.

Copper will go into the residue first, as it may be precipitated by cadmium as well:



In commercial practice, however, the two are precipitated together and separated in another recovery cycle.

The copper-cadmium residue consists of particles of copper and cadmium, excess zinc dust and solid particles of the gangue entrained from the thickener by the neutral solution.

The composition, in percentage, of the copper-cadmium residue follows:

Copper	2-8
Cadmium	6-12
Zinc	30-40

The copper-cadmium purification residue is a valuable source material for the manufacture of cadmium, with copper removed as a by-product. The residue also collects the rare metals thallium and indium.

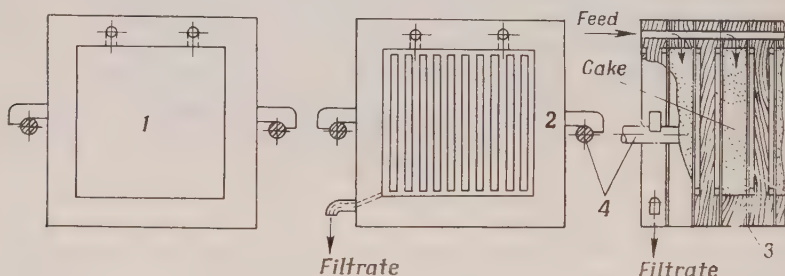


Fig. 136. Filter press:

1—frame; 2—plate; 3—filter cloth; 4—guide

Zinc-dust purification under commercial conditions is carried out in mechanically agitated tanks with a capacity of 35 to 45 cu m. The tanks are filled with the overflow solution from neutral thickeners without auxiliary heating (38 to 40°C). At the start of each purification a small quantity of zinc dust is added, and the solution is agitated for 40 to 50 minutes. The purifying tank discharge is pumped to filter presses (Fig. 136).

A filter press is a batch apparatus to which the pulp to be filtered is fed under a pressure. The cake formed has to be removed by hand, for which reason the use of filter presses is only warranted where small quantities of solids have to be separated from considerable volumes of liquid. A filter press consists essentially of frames and filter plates. A filter plate is a rectangular piece of wood, metal or plastic material 20 to 50 mm thick. Within some distance of its edges, parallel grooves are made, joined together by horizontal grooves. The size of a plate is the same as that of the frame. One of the side walls of the plate is fitted with a cock to drain the filtrate. At the top both the frames and the plates have 2 to 4 holes. In the

frames the holes communicate with the inner space. The frames and plates are mounted alternately, with a filter cloth placed between each frame and plate. The round holes at the top are aligned to form a cylindrical passage. Similar holes are cut in the filter cloths. An assembly of 10 to 60 frames, plates and filter cloths is clamped in a support by a screw or a hydraulic clamp. The pulp to be filtered is fed by a pump under a pressure of 1.5 to 4 atm into the cylindrical passage from which it finds its way into the space between two parallel filter cloths. The solution passes through the pores in the cloth, flows down the grooves in the plates to the cock and into a drainage launder. After the filter is filled with the residue, it is taken apart, and the residue removed.

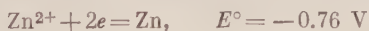
The clarified solution is further treated for the removal of cobalt with sodium xanthogenate and blue vitriol. The cobalt content of the solution can be easily brought down to 4 milligrams per litre. The cobalt residue carrying about 4 per cent Co may be used for the manufacture of cobalt.

The purified solution is treated for the elimination of chlorine after its content has risen to 100-150 milligrams per litre. Chlorine may come from running water or chlorine-bearing recycled materials. During electrolysis, ions of chlorine bring about severe corrosion of lead anodes and contaminate the cathode deposit with lead. The rapid deterioration of coolers is likewise due to the presence of chlorine. The removal of chlorine is based on the precipitation of nearly insoluble chlorides of copper, silver or mercury. Copper purification is used in most cases; the reagent is freshly deposited cement copper.

86. The Electrolysis of Zinc Sulphate Solution

The purified neutral solution subjected to electrolysis contains ions Zn^{2+} , SO_4^{2-} , H^+ and OH^- .

Both ions of zinc and hydrogen can discharge at the cathode:



On the basis of their electrode potentials, it would appear that the electrolysis of zinc sulphate solution would result simply in the decomposition of water with the production of hydrogen at the cathode. This is not the case, however, and zinc is successfully recovered by electrolysis of aqueous electrolytes.

The explanation lies in that the actual potential to deposit hydrogen at a zinc electrode is much higher than the theoretical value. This difference is called the hydrogen overvoltage of a zinc electrode.

The hydrogen overvoltage is due to the fact that hydrogen ions have a lower rate of discharge than have zinc ions.

It is essential to reduce hydrogen production at the cathode, for this improves the current efficiency of electrolysis. To this end, all factors that tend to increase the hydrogen overvoltage on zinc should be utilised where possible.

The discharge potential of zinc ions is very close to that determined by the Nernst equation:

$$E_{\text{Zn}} = E^\circ + (RT/nF) \ln f_{\text{Zn}} C_{\text{Zn}} \approx -0.76 + 0.029 \log f_{\text{Zn}} C_{\text{Zn}}$$

where E° = electrode potential;

C_{Zn} = zinc concentration in electrolyte;

f_{Zn} = activity of zinc ions.

The discharge potential of zinc ions grows more positive as their concentration (or, rather, their activity) in the solution increases.

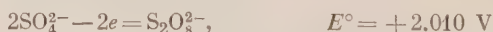
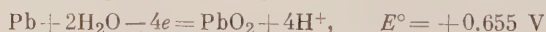
The discharge potential of hydrogen ions is the sum of the equilibrium potential and overvoltage:

$$E_{\text{H}} \approx 0.058 \log f_{\text{H}} C_{\text{H}} + \eta,$$

where η is the overvoltage, V.

The equilibrium potential increases with decreasing pH, while hydrogen overvoltage rises with increasing current density and decreasing temperature. Putting it another way, for higher current efficiencies in electrolysis use should be made of concentrated electrolytes of the least possible acidity, and electrolysis should be conducted at high current densities and low temperature.

The following electrochemical reactions are possible at the lead anode of the electrolytic bath:



From the standard electrode potentials it follows that the first to form is lead sulphate which produces a thin film of nearly insoluble crystals on the anode. The area of the lead electrode is, as a result, decreased, the current density rises, and so does the anode potential. The next to form in the pores of the lead sulphate is PbO_2 followed after another increase in the anode potential by the release of oxygen—the principal reaction at the anode. The SO_4^{2-} ions can discharge to form persulphuric acid only at extremely high current densities practically unattainable.

Energy consumption in the electrolysis of zinc is much greater than in the electrolytic refining of copper or nickel, for some of it is spent to sustain the chemical reactions. Nevertheless, energy consumption per ton of cathode zinc may be determined from the relationship common to all cases of electrolysis (Faraday's Law of electrolysis), as follows:

$$\frac{\frac{10^6}{65.38}}{2} \times 26.8 \text{ A-h per ton of cathode zinc}$$

and energy consumption will be:

$$W = \frac{10^6 \times 2 \times 26.8}{65.38} \times \frac{V}{K_T} = 0.818 \times 10^6 \times \frac{V}{K_T} \text{ Wh/ton}$$

$$W = 0.818 \times 10^3 \times \frac{V}{K_T} \text{ kWh/ton}$$

where W = energy consumption, kWh/ton;

V = voltage across the electrolysing cell, V;

K_T = current efficiency.

The voltage applied to the cell is the sum of the electrode potentials and the voltage drop across the cell:

$$V = (E_a - E_k) + IR$$

where E_a , E_k = anode and cathode potentials, respectively;

I = amperage;

R = total resistance of the cell, including the resistance of the electrolyte, electrodes and contacts.

The applied voltage, V , is mainly governed by the current density and the resistance of the electrolyte. An increase in the current density increases the anode overvoltage of oxygen and, consequently, the value of E_a . At the same time, there is an increase in IR . The value of IR may be reduced by a closer electrode spacing, increased temperature, and the increased concentration of sulphuric acid in the electrolyte.

The factors affecting current efficiency have been discussed elsewhere and they are opposite to those governing the applied voltage (they call for increased current density, reduced temperature, and reduced acidity of the electrolyte).

As electrolysis progresses, the zinc concentration in it is reduced, its acidity increases, and current efficiency decreases, making the complete recovery of zinc from the electrolyte economically unattractive. The usual practice is to withdraw the electrolyte from the cell after about half the zinc has been recovered and the equivalent

amount of free sulphuric acid has been regenerated. The depleted electrolyte is then used to leach roasted concentrate. The zinc left in the spent electrolyte, though not lost altogether, is a ballast on the process. From this point of view, it is desirable to keep the amount of zinc left in the electrolyte to a minimum.

Obviously, the least energy consumption can be obtained when an optimum balance of all the factors involved is struck. Many years' experience has resulted in what is known as the standard method of zinc electrolysis, currently employed by the majority of Soviet zinc producers. In the standard method, current densities lie between 400 and 600 A/sq m. The original electrolyte contains 110 to 130 grams per litre of zinc, while the composition of the spent electrolyte is 100 to 150 grams per litre of free sulphuric acid and 40 to 60 grams per litre of zinc. The roasting and leaching as described above are in keeping with the standard method.

The impurities copper, nickel and cobalt depositing together with zinc at the cathode, may seriously lower the hydrogen overvoltage at those points. "Local-cell" action may result which will prevent the deposition of zinc in the vicinity due to hydrogen evolution. Pores and through holes may form near the deposited impurities, the area of the deposit will increase, while both density and current efficiency decrease, especially when there is a considerable build-up of sulphuric acid in the electrolyte. Furthermore, impurities in the cathode deposit contribute to the redissolution of zinc (Table 38).

Table 38

Evolution Potentials of Hydrogen on Some Metals and Zinc Corrosion in the Presence of Impurities of These Metals

Metals	Standard electrode potential, V	Evolution potential of hydrogen at 400 A/sq m, V	Zinc corrosion at an impurity content of 10 mg/lit, g/sq m-h	Ordinary impurity content in electrolyte, mg/lit
Zinc	-0.76	-1.10	40	—
Iron	-0.44	-0.55	—	10-30
Nickel	-0.23	-0.44	490	0.5
Cobalt	-0.26	-0.48	340	1-25
Arsenic	0.3	—	360	0.1
Antimony	0.2	-0.79	870	0.05-0.30
Copper	0.34	-0.68	850	0.4-1.0
Cadmium	-0.40	-0.84	220	—
Lead	-0.13	-1.20	430	0.1

Iron when present in the electrolyte reduces current efficiency. At the cathode, ferric iron is reduced to ferrous iron, while at the anode it is again oxidised. This action consumes power that would otherwise be used to deposit zinc.

The presence of cadmium and lead has little effect on current efficiency, but the slab zinc will be contaminated by them. The appearance of lead ions in the electrolyte is an indication that there is a build-up of chlorine ions which cause corrosion of the anodes.

The harmful effects of some impurities may be moderated by the addition of surface-active materials to the electrolyte. These addition agents may be glue, goulac and various organic substances. Most often, up to 0.1 gram of glue per litre is added for the purpose. This, however, does not make solution purification unnecessary.

Addition agents, especially colloids, also have a wholesome effect on the physical character of the zinc deposit—a factor important to both the progress of electrolysis and subsequent zinc smelting. A rough, porous, loose or perforated deposit has a greater surface area than a smooth and dense one, for which reason current density, hydrogen overvoltage and, consequently, current efficiency in the former case will be lower than in the latter. Furthermore, the dendritic crystals (known as “trees” among zinc makers) tend to grow on projections at right angles to the cathode surface and towards the anode and may cause short circuits in the zinc cell. Both troubles are efficiently eliminated by adding colloids. Migrating through the electrolyte, they deposit on any projections or points of crystal growth because the current density there is higher than on the normal surface. By an insulating action, the clusters of colloidal particles thus deposited reduce the amount of current to those points and the surface of the deposit is smoothened.

The cells or tanks used in the electrolysis of zinc are made of concrete or wood. On the inside they are lined with lead plate, acid-resisting lutes, rubber, acid-proof brick or, more recently, with PVC sheets as a protection against corrosion. On the outside cells are given a coat of varnish, bitumen or PVC sheeting for longer service life. Wooden tanks are cheaper than those from concrete but their service life is much shorter.

Cells are mounted on concrete pillars up to 6 m high from which they are insulated by non-absorbing materials such as glass or porcelain blocks. Most plants arrange cells in cascades of 20 to 25 cells each. Two such cascades may be placed side by side to form a double cascade. The adjacent tank may even be built as a double tank with a common wall.

Anodes are cast from a lead-silver alloy containing 1 per cent silver as well as small additions of thallium, cobalt, arsenic and some other metals which serve to slow down the corrosion of anodes.

They are made either of grid or wafer construction in order to increase their surface area and thus to reduce current density and to improve circulation within the cell. Anodes are usually 6 to 8 mm thick, the other dimensions being as shown in Fig. 137.

The header bars used to support the anode sheets are usually copper bars covered with lead. They are welded to the top edges of the anodes. The anodes are held in proper relation to each other by means of PVC spacers or edge strips.

Cathode plates are cut from rolled and ground aluminium sheets of high purity. The cathodes are normally 20 to 25 mm larger than the anodes. The sheets are welded to support, or header, bars of aluminium with a copper contact at one end. At the edges they

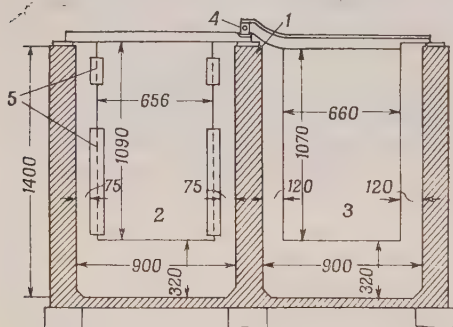


Fig. 137. Section through a double electrolyzing cell:

1—common wall; 2—anode; 3—cathode;
4—anode/cathode contact; 5—edge strips
of PVC

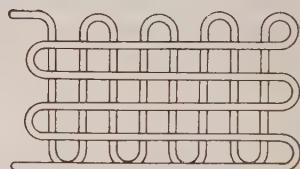


Fig. 138. Electrolyte-cooling coil

are fitted with U-shaped rubber or PVC edge strips which facilitate the removal of the zinc deposit from the cathode plate.

A zinc cell usually contains 28 to 30 cathodes and anodes, spaced at 28 to 35 mm, so placed that their header bars rest on the sides of the cells. For electrical contact, the ends of the cathode header bars are placed on the anode header bars on the adjacent cell (Fig. 137). In fact, copper buses are only required at the outer cells of each unit.

Within a unit the cells are usually connected in series. The total voltage across the unit is the cell-voltage multiplied by the number of cells in it. Therefore, the number of cells in a unit is determined by the maximum voltage available from the equipment and the voltage drop across the supply circuit.

The d.c. power required for the electrolysis of zinc is usually

supplied by mercury-arc rectifiers which operate at a much higher efficiency than motor-generator sets. The current in a zinc-cell unit is usually 10,000 to 15,000 A and the voltage across the unit is 500 to 650 V.

The neutral purified solution to be electrolysed is fed by gravity to individual units from a feeder tank down PVC pipes or launders, and distributed between the individual cells within each unit by rubber hoses fitted with clamps. Depleted electrolyte is removed from the cells on the opposite side through a drain pocket and a launder which carries it to a sump whence the spent electrolyte is directed to the acid leach step.

A considerable amount of heat must be dissipated if the cells are to operate within the optimum range of current efficiency. To maintain the temperature within the cells between 30° and 35°C, fresh electrolyte is cooled either before it is fed into the cells or in the cells. In the latter case, use is made of flat lead or aluminium coils installed at the front end of each cell (Fig. 138), where fresh electrolyte enters the tank. External cooling is more advantageous, because the cooling coils take up some of the useful space in the cells. Most promising in this respect are vacuum-evaporation units which are coming into use. For their operation these units depend on boiling the electrolyte in a vacuum where it gives up its latent heat of evaporation.

The servicing of a zinc-electrolysing plant includes watch on the operation of the cells, removal of zinc from the cathodes, replacement of the anodes, and removal of anode sludge. Supervision of cell operation includes the control of cathode-to-anode voltage, electrolyte temperature, and electrolyte composition. An increase in the cell voltage is an indication that the contacts have grown dirty and need cleaning. A sharp drop in, or disappearance of the voltage across the cell, points to a short circuit, which should be cleared up immediately.

The zinc deposit is stripped once a day from five to seven cathodes at a time. The operation is usually performed on machines. The removal of cathode deposits may be facilitated by adding a small quantity of soluble antimonates to the electrolyte. The zinc deposits thus removed are sent to a casting division for melting, and the cathode plates are wire-brushed and slipped back into their cells. Anodes usually remain in service for eighteen to twenty-four months.

Periodic removal of the manganese sludge is important because its accumulation increases electrolyte resistance at the anodes. The manganese sludge consists of about 70 per cent MnO_2 , 10 to 14 per cent Pb and up to 2 per cent Zn. It is utilised in the neutral leach in order to oxidise the iron.

The oxygen bubbles produced at the anodes entrap droplets of electrolyte. If adequate precautions are not taken, a heavy spray of acid may rise from the cell, producing a mist in the shop which may corrode the equipment, affect the skin and respiratory tract of the workmen and destroy their teeth. The mist from the cells may be effectively kept down by a froth maintained in the top of the cells. To this end, a mixture of cresylic acid, sodium silicate and gum arabic is added.

87. Melting of Cathode Zinc

When melted, some of the cathode zinc is lost due to oxidation, especially if the cathode deposit is not sufficiently smooth and dense. To reduce the oxidation loss, smelting should be conducted at the lowest possible temperature, taking care to protect the metal from atmospheric oxygen. At elevated temperature zinc is easily oxidised even by carbon dioxide. The oxide film separates individual droplets of molten metal from one another, preventing them from coalescing and dross is formed on the surface of the molten metal. Dross production may be reduced by an addition of ammonium chloride which decomposes on heating into ammonia and hydrogen chloride. The latter reacts with zinc oxide to form molten zinc chloride (with a melting point of 318°C) which has a greater surface tension. When exposed, droplets of molten zinc coalesce easily.

Until recent years, cathode zinc was mainly smelted in reverberatory furnaces in which 4 to 5.5 per cent of the cathode weight was usually lost to dross and flue dust.

In the past few years, induction melting has shown considerable promise. The loss of zinc to dross and dust in the case of induction melting does not exceed 2.5 per cent owing to a well sealed furnace space and the absence of gas flow. The requirements in ammonium chloride are 0.4 to 0.8 kg per ton of zinc, which is half the amount required for reverberatory zinc melting. Energy consumption averages about 110 kWh per ton of zinc.

Molten zinc may be cast into slabs either mechanically on casting wheels and straight-line machines, or by hand using dippers with long handles carried by crawls and chains. A slab of zinc thus cast has the shape of a truncated rectangular pyramid weighing 20 kg.

Dross contains about 85 per cent Zn (of which quantity 25 per cent is in metal form and 75 per cent as oxides). The dust catch consists of ammonium chloride and zinc chloride. The dross and dust are re-treated in a separate recovery cycle in order to avoid the contamination of the solution with chlorine.

sumption, which is the second most important factor affecting the economics of zinc production, will be:

$$W = 0.818 \times 10^3 \times \frac{3.50}{0.95} = 3055 \text{ kWh/ton}$$

The actual energy consumption varies from plant to plant and may be anywhere from 3100 to 3300 kWh/ton. The total energy consumption is about 4000 kWh/ton.

Table 39

**Balance Sheet of Zinc Hydrometallurgy
from Green Concentrates**

Item	Zinc, per cent
Slab zinc	87.00
Residues as:	
ferrites	7.86
sulphides	3.35
silicates	0.21
oxides	0.03
sulphates	0.05
Irrecoverable mechanical losses	1.50
Total	100.00

Slab zinc contains 99.97 to 99.99 per cent Zn, the remainder being impurities cadmium, lead, iron and copper. The composition answers the requirements of the relevant U.S.S.R. State Standard for Grades II0 and II1.

Some plants use high current densities in the range 1000-1100 A per square metre of cathode area and concentrated electrolytes containing up to 215 grams of Zn per litre. Owing to the increased current density, the ampere efficiency is maintained high even in the case of a considerable build-up of sulphuric acid (250 to 300 grams per litre). This, however, involves greater outlays for cooling. Leaching is carried out in mechanically agitated steam-heated batch reactors. The source concentrate may be roasted at temperatures up to 1000°C, as the ferrite produced will for the most part pass into solution.

The advantages of high-density working are increased throughput in roasting, leaching and electrolysis and a more compact equipment owing to the fact that a smaller volume of solution has to be handled

and there is no residue to re-treat. Still, high-density working has not yet found any appreciable use because of the severe wear caused to the equipment by strong acid solutions, the necessity to steam-heat the solution in leaching, and to cool the electrolyte in the zinc cells. At the time of this writing, only two zinc producers in the world, with an aggregate zinc production of about 70,000 tons a year, were using this method.

Other schemes standing in between the low- and high-density methods use the batch leaching of roasted concentrates in mechanically agitated tanks. The batch system is advantageous when treating diversified feed as each batch can be held for testing and the leaching conditions may be adjusted accordingly.

In single leaching, the initial cost of equipment is much lower than in double leaching. The excess acid is neutralised with lime-rock, and the calcium sulphate thus formed passes into the residue.

89. Horizontal Retort Practice

A brief outline of the equipment employed in horizontal retort practice is given in Sec. 82 and so only a few more points will be added in this chapter.

Condensers and especially retorts must be fire-resistant, strong and impervious to zinc vapours. A retort which has developed even the tiniest crack must be immediately replaced, or zinc loss would be inevitable.

Because of the fragility, retorts and condensers cannot be shipped over great distance. This is the reason why they are made at a pottery within a zinc smelter.

Retorts and condensers are extruded from a damp and well-plugged mixture of fireclay, grog and coke. Green retorts and condensers are dried and fired to make them strong and fire-resistant. The shape and dimensions of retorts and condensers are shown in Fig. 140.

As the art of zinc smelting stands at present, the production of 100 tons of zinc a day requires over 3000 retorts. At one time, use was made of distillation furnaces holding up to 1000 retorts. They have proved cumbersome and been replaced by furnaces holding 240 retorts.

Fig. 141 shows a cross section through such a distillation furnace. The retorts are stacked in vertical rows. Their closed ends rest on shelves inside the furnace, while their open ends, or noses, stick out of the furnace through openings. The retorts are inclined towards their noses.

The main difficulty in distillation furnace design is that the high temperature required for operation has to be distributed uniformly

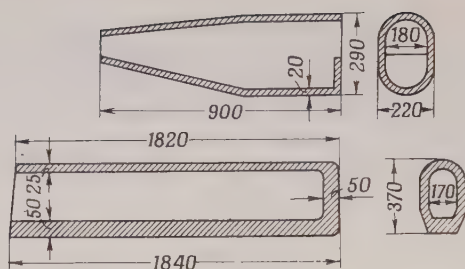


Fig. 140. Retort and condenser

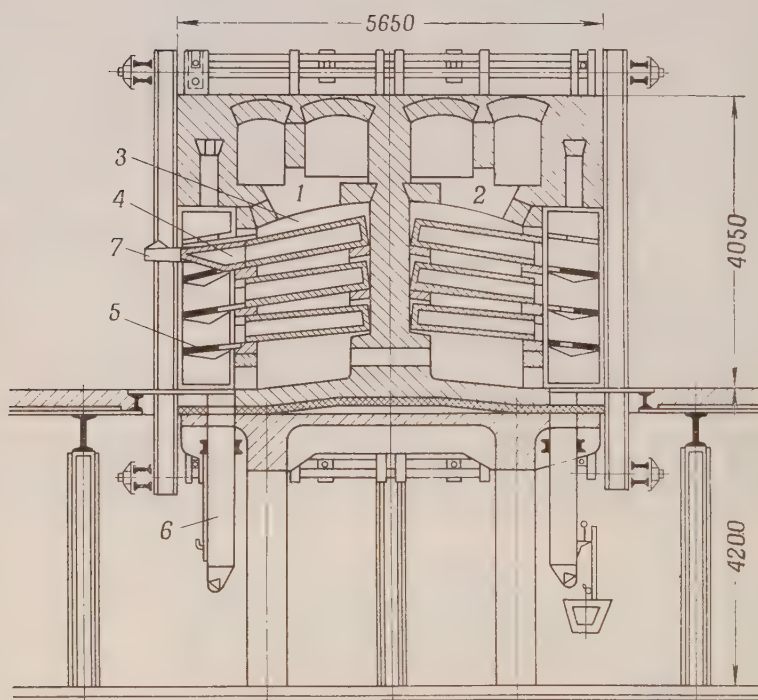


Fig. 141. Cross section through a zinc distillation furnace:
 1, 2—gas and air flues; 3—retort; 4—condenser; 5—cast-iron condenser shelves;
 6—discharge chutes for retort residue; 7—prolong

throughout the furnace space. This has necessitated the use of gaseous fuel, usually producer gas. Before the gas and air are fed into the furnace, they are preheated in checkerwork preheaters or regenerator chambers similar to those used in open-hearth steel furnaces. The preheaters are located either beneath or at the end of the retort furnace. The sides of the furnace have recesses and cast-iron shelves to support the condensers which are attached to the mouths of the retorts. Under each condenser there is a round hole in the shelf. The hole is located against the mouth of the respective retort and serves to remove the hot residue from the retorts at the end of each run.

The size of a retort furnace varies with its construction. Three-row furnaces for 240 retorts measure about 20 m in length, 5.3 to 5.5 metres in width, and 6.8 m in height. The bottom of the furnace is 2.75 m above the floor level of the shop.

Running at the roof of the furnace parallel with its long axis are two pairs of flues. In each pair, one flue is for the gas and the other for the combustion air. Between the respective regenerator chambers and the flues are placed hydraulically operated valves by which the combustion gases and the waste gases can be led to and from the furnace and to the stack, and reversed periodically as desired, much as is done in open-hearth furnaces. The reversals of the gases make it possible to maintain a uniform temperature of about 1400°C in the retort furnace.

The basic reaction of zinc distillation is the reduction of solid zinc oxide with gaseous carbon monoxide. For the reduction and distillation to proceed at a sufficiently high rate, the grains of the concentrate should be small, as this increases the surface area of the zinc oxide exposed to the reducing agent. Too fine a concentrate, however, would form a very dense bed in the retort, obstructing the escape of zinc vapours. Furthermore, local accumulations of zinc vapours may eject the charge out of its retort.

A favourable range of grain sizes of the charge may be obtained by sintering or nodulising the zinc calcine and regrinding the sinter to 3 or 4 mm.

The zinc calcine must contain as little sulphide and sulphate sulphur as possible, which requirement can be met by roasting the concentrate at much higher temperatures than is customary in zinc hydrometallurgy. The formation of zinc ferrites is no limiting factor, since the zinc from them can be driven off as easily as from ordinary zinc oxides.

As in lead metallurgy, green zinc concentrate is roasted in two stages, since single-stage blast roasting would not give good elimination of sulphur due to the formation of low-melting eutectics which bring about premature sintering. The first stage is conducted

in fluidised-bed furnaces at relatively low temperature so as to eliminate the bulk of the sulphur and to avoid sintering. The second stage is carried out at 1100 to 1200°C on sintering machines until the remaining sulphide and sulphate sulphur is eliminated and a porous sinter is obtained. The chemistry of and conditions for the first stage are about the same as in zinc hydrometallurgy.

The discharge from the first stage still contains some sulphur, and fuel is seldom added to the sintering charge. Fuel consumption does not exceed 3 to 3.5 per cent of the first-stage product. The sintering charge is wetted down to 6 to 10 per cent moisture in order to reduce dust formation and to improve gas passage through the material.

At some plants, sodium chloride is added to the sintering charge so as to fume the lead and cadmium from the zinc concentrate. The volatile PbCl_2 and CdCl_2 thus produced are recovered by dust catchers. At the same time, some zinc is driven off as ZnCl_2 . With properly adjusted sintering conditions, up to 80 per cent lead and cadmium may be fumed from the concentrate into a rich dust. Fuming sintering facilitates concurrent elimination of impurities and improves the subsequent distillation of zinc.

By another method, zinc concentrate is roasted in a fluidised bed in a single run at 1100 to 1200°C so that only 0.5 to 0.8 per cent sulphur is left in the sinter, over 95 per cent lead and cadmium fumed off, and a sintered calcine suitable for distillation obtained. The fumes carrying 17 to 24 per cent Pb and 3 to 5 per cent Cd are recovered by dust catchers.

The travelling-grate sintering machines employed for second-stage roasting are similar in construction to those used in the metallurgy of iron, nickel and lead. Their throughput, however, is lower and seldom exceeds 15 tons per square metre of windbox area a day, the reason being that zinc sulphide burns slowly, ZnSO_4 is difficult to decompose, and the bed is of relatively low bulk density.

The sinter discharged from the sintering machines is crushed in rolls and graded into grain sizes. The material larger than 5 mm forms the bed on the sintering machines. The fine material under 1 mm is returned to the sinter charge, and the intermediate grain size is used for zinc distillation.

In sintering, carry-over dust amounts to 3 or 4 per cent of the charge weight and is therefore passed through electrostatic precipitators. The recovered dust contains 20 to 35 per cent Pb and 0.4 to 1.6 per cent Cd and is re-treated separately for the recovery of its values.

The next step in zinc distillation is the mixing of the sintered calcine with reduction fuel. The most common reducing agents

are pulverised anthracite coal ground to 1-6 mm to which up to 50 per cent coke breeze is added. In addition to its duty as a reducing agent, the coal separates the concentrate particles and prevents the formation of low-melting mixtures. As a result, the retort residue is loose and can be easily withdrawn from retorts.

The proportion of coal in the retort charge is about three times the quantity required for the reduction of the oxides. Practically, it accounts for 35 to 40 per cent of the charge weight. The charge is agitated by mechanical stirrers and delivered to the distillation

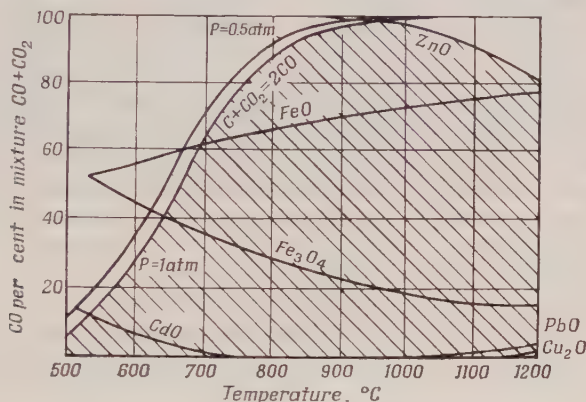
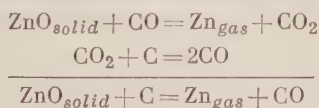


Fig. 142. Diagram showing the conditions required for zinc reduction by carbon (cross-hatched portion gives the conditions obtained in retorts)

division by conveyers. After the retorts are hand-charged, the condensers are set up and luted in place with a wet mixture called "loam", and prolongs (or blue-powder pans) are put some time after.

The atmospheric oxygen left in the retort after charging is soon spent to burn the coal; the nitrogen and other gases are ousted from the retort and the pores of the charge by products of combustion; and so only a mixture of CO, CO₂ and metal vapours is left in the retort.

As follows from the chart of Fig. 142, the reduction of zinc begins at about 950°C and proceeds according to the reactions



At 1100 to 1150°C, the CO₂ content in the equilibrium gas mixture is negligibly small in comparison with the content of CO in it. The total pressure in the retort is but slightly above 1 atm (abs).

Therefore, $p_{\text{Zn}} = p_{\text{CO}} = 0.5$ atm (abs). Actually, the partial pressure of zinc vapours is somewhat lower than 0.5 atm (abs), since some of the CO_2 is produced by several concurrent reactions in which the oxides of impurities are reduced.

The optimum composition of zinc calcine depends on the composition of green concentrate and the conditions under which it is roasted.

An approximate composition of zinc calcine follows (in per cent):

ZnO	55.8	PbO · SiO ₂	0.7
ZnO · Fe ₂ O ₃	23.8	SiO ₂	3.6
ZnS	2.8	Al ₂ O ₃	2.8
Fe ₂ O ₃	6.1	CaO + MgO	3.9

The higher iron oxides begin to be reduced to FeO at 640°C. Some of the FeO reacts with the silica of the charge to form a relatively insoluble silicate, and the balance of the FeO may be reduced to Fe. The iron picks up carbon and turns to pig iron which may sometimes be smelted from the charge. The reduction fuel keeps the droplets of molten iron apart, and so large pieces of pig iron in the distillation residue occur seldom.

The impurities copper, cadmium and lead are easily reduced at the beginning of the cycle because of weak affinity for oxygen.

Silica, alumina and alkali-earth oxides cannot be reduced under conditions of zinc distillation. However, their relative and absolute proportion in the charge has an important effect on distillation. The oxides, especially in the presence of FeO and PbO, can form low-melting alloys. Molten silicates make the distillation residue very dense and sticky, difficult to rake out. Furthermore, in melting they can burn through the retort walls. In this respect, the presence of much lead and iron simultaneously with much silica is especially undesirable. Sometimes, the low-melting ash of the coal may cause damage to the retort and bring about the formation of a hard-to-remove residue.

As it has a high vapour pressure (Table 40), the zinc of the retort charge readily vaporises to liquefy from the retort gas in the condenser. The distilled cadmium is also collected in the condensate.

Liquid zinc separates out of the retort gas as a slowly coagulating metallic fog at 830 to 870°C. The equilibrium of vapour pressures above the droplets is attained at a lower temperature than over the flat surface of the molten pool. The retort gas remains in the condenser for 13 to 15 seconds, and the zinc vapour that escapes from the condenser into the prolong is precipitated there as powder due to rapid cooling.

The incomplete condensation of zinc vapours in the condenser is also due to changes in the composition of the retort gas with

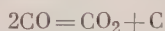
Table 40

Pressure of Metal Vapours in Zinc Distillation

(As found from approximate equations)
mm Hg

Metal	Middle of retort	Retort mouth	Condenser	Prolong
	Average temperature, °C			
	1150	1000	550	200
Cadmium	17,000	6080	35	10^{-7}
Zinc	6030	1830	4	10^{-11}
Lead	9	1	10^{-4}	—
Iron	10^{-3}	10^{-6}	—	—
Copper	10^{-3}	10^{-4}	—	—

cooling. The ratio of CO to CO₂, which is at equilibrium at the temperature of the retort, is shifted towards a greater partial pressure of CO₂ due to the dissociation of CO:



The carbon dioxide partly oxidises the zinc vapours in the condenser:



When droplets of molten metal have experienced superficial oxidation they fail to coalesce, and blue powder is formed in the condenser.

The zinc vapours, condenser blue powder, zinc oxide and soot that escape from the condenser precipitate in the prolong to form prolong blue powder which contains 60 to 70 per cent metallic zinc and 13 to 15 per cent zinc as oxide and carbonate.

Cadmium is reduced in the retort before zinc and is more volatile, for which reason the partial pressure of cadmium vapours is higher at the beginning than at the end of the distillation. Although the dew point of cadmium is much lower than the temperature of the condenser due to low concentration, a good proportion of the cadmium is precipitated in the condenser together with the bulk of the zinc. Very little cadmium vapour reaches the prolong.

The solubility of cadmium in zinc promotes the precipitation of cadmium together with zinc, and the equilibrium vapour pressure of cadmium is reduced. The cadmium content is so divided that 60 to 80 per cent goes to the pool of molten zinc in the condenser, and 20 to 40 per cent in the prolong dust.

Lead is reduced in the retort even more eagerly than cadmium. It is of low volatility, however, and only 20 to 25 per cent Pb goes into vapours. Nevertheless, this quantity is sufficient to add to the impurities in the zinc and prolong dust. The lead content of the distillation products increases as retort temperature rises.

Copper, iron and other impurities are practically non-volatile and can only be carried over from the retort into the condenser mechanically. Therefore, they are present in distilled zinc to a limited degree.

The retort residue carries 10 to 13 per cent of all zinc, gold, silver and copper as well as excess reduction coal and is usually re-treated for the recovery of its values.

Investigators differ as to the optimum composition of the retort residue. In some cases, it has been found to contain 12 to 60 per cent of all zinc as zinc sulphide. According to Volsky and Slobodskoi (both of the U.S.S.R.), the percentage composition of the retort residue at one zinc smeltery was as follows:

Zinc sulphate	0.1	Zinc ferrite and zincate	18.9
Free zinc oxide	32.1	Zinc sulphide	15.2
Zinc silicate	23.4	Zinc aluminate, etc.	10.2

Silicates, ferrites, zincates and zinc aluminates are salts of weak acids and weak bases. Their standard free energy changes are insignificant, and so the conditions for their reduction must not differ materially from those for the reduction of free zinc oxide. Their incomplete reduction is presumed to be mainly due to the superficial fusion of the charge particles before the zinc has been reduced and driven off. The fused surfaces shut out reducing gases, and the rate of zinc reduction slows down.

The temperature in the charge near the retort mouth is lower than elsewhere in the retort; the reduction proceeds there at a lower rate, and the residue at the front ends is always higher in zinc, for which reason it is termed the rich crust.

The material that goes to make retorts has a direct bearing on the efficiency of zinc distillation. If the retort clay is of low refractoriness, a lower temperature has to be maintained in the retort furnace; the rate of reduction will slow down; and the recovery of zinc will not be so complete.

A distillation, or firing, cycle usually occupies 18 to 20 hours. During this period, the molten zinc is drawn from the condensers at regular intervals so as to avoid their overloading. In most cases, the first draw is made 6 hours after the charging manoeuvre, the second draw after 12 hours, and the final draw after 18 hours.

The rate of distillation is at its highest at the beginning of a firing

cycle, and the first draw usually contains about 60 per cent of the zinc present in the charge. The second draw accounts for about 30 per cent and the final draw for the remaining 10 per cent of the zinc in the charge. The zinc of the first draw is high in cadmium and is relatively low in lead. The zinc of the final draw carries almost no cadmium and most of the lead present in the charge.

The charging manoeuvre requires up to 6 hours and includes the drawing of the last zinc from the condensers, the removal and disposal of the retort residues, the emplacement of the new mixed charge, and the replacement of unsound retorts.

Distillation Products and Their Re-treatment. Distilled zinc contains 98-99 per cent Zn, up to 4.8 per cent Pb, 0.05 to 0.1 per cent Fe, 0.004 to 0.02 per cent Cu and 0.2 to 0.4 per cent Cd. It can only meet the requirements for the lowest grades and has to be refined.

Prolong dust consists of finely divided particles measuring a few microns in diameter. It carries from 0.7 to 2.3 per cent cadmium and is therefore re-treated for cadmium recovery.

Condenser dust is produced in limited quantities and carries about 0.1 per cent of all zinc and the impurities mechanically carried off with the gases. Condenser dust is usually returned to the retort with a new mixed charge.

The retort residue is re-treated for the recovery of zinc, lead, copper, and the precious metals. The methods employed for the purpose are discussed elsewhere.

Broken condensers are also re-treated for the recovery of zinc. The point is that during a firing cycle, a rich crust of zinc oxide and metallic zinc is formed on the inside of the condensers. Some of the molten metal is absorbed by the pores. The surface crust is usually removed by hand, but the clay still contains up to 15 per cent Zn. Therefore, the mechanically cleaned clay is ground down to 1 to 3 mm and dressed on concentration tables. The 60-70 per cent zinc concentrate thus obtained may be recharged into the retorts. The tabling tails are re-treated in company with the retort residues.

Broken retorts are inevitable, for the service life of a retort is 15 to 25 days at the most. Zinc vapours penetrate the retort walls to be oxidised by the furnace gases moving towards them, and the resultant zinc oxide reacts with the wall material. In the long run, the retort walls collect high-melting zinc aluminates and silicates, so that broken retorts carry up to 7 per cent Zn. The fragments rich in zinc are picked out by hand and are re-treated together with the retort residues and other by-products.

The loam with which the condensers are fitted to the retorts also grows zinc-saturated during the distillation cycle. Therefore it is

removed, sorted out by hand, the droplets of metal are remelted, and the remaining material is recharged.

An approximate percentage break-down of distillation products follows:

Distilled zinc	82.8
Prolong dust	4.8
Retort residue	6.3
Broken condensers	1.1
Broken retorts	0.7
Loam	3.2
Losses with gases	1.1
Total	100.0

90. The Vertical Retort Process

The basic disadvantages of the horizontal retort process are its intermittent nature, cumbersome furnaces, and difficulty of mechanisation. They have been to some extent eliminated in the vertical retort process which operates continuously and uses carborundum retorts.

Carborundum, or silicon carbide (chemical formula SiC), is a refractory with a melting point of over 2700°C . In the manufacture of refractories, powdered carborundum is mixed with 6 to 12 per cent (by weight) of fireclay. The batch thus obtained is wettened, pressed in moulds, dried and fired at 1400 to 1600°C . The refractories retain mechanical strength up to 2000°C , are chemically neutral and are 3 to 4 times as heat-conductive as grog.

A vertical retort is a shaft rectangular in cross section. It is made either of silicon carbide slabs or silicon carbide bricks, as shown in Fig. 143.

The retort is fired with producer gas which is burned in chambers on either side of the retort. The heated portion is about 7.5 m high, while the internal dimensions may be 0.3 m by 2.2 m. The charge is introduced in the form of briquettes from above through a firebrick chamber called the "charge column" which also serves to provide an escape for zinc vapours. The bottom portion of the retorts terminates in a residue extraction mechanism which is an iron box fitted with a water seal. The spent residue is discharged continuously and retains the original shape of briquettes.

The briquettes are prepared from a mixture of roasted zinc concentrate, anthracite, coking coal and suitable binders such as coal tar. After thorough mixing, the batch is passed through a briquetting press, and the briquettes are heated to 750 - 900°C . The coal and tar are coked, and the briquettes attain a strong and porous structure.

The chemistry of the vertical process does not differ from that of the horizontal retort process. The rate of heat transfer through

the silicon carbide walls of the vertical retort and the briquetted charge is higher than in ordinary distillation, and so zinc recovery is more complete, and its content in the retort residue is usually under 3 to 5 per cent.

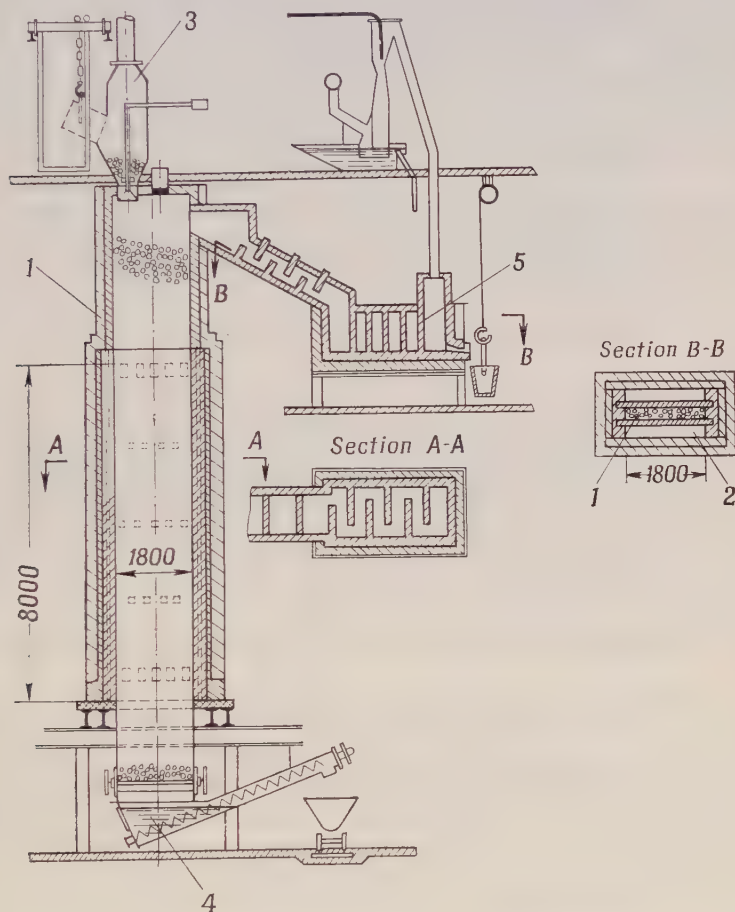


Fig. 143. Scheme for the continuous vertical retort process:

1—retort; 2—gas combustion chamber; 3—charging device; 4—discharging device; 5—condenser

The normal life of a vertical retort is 3 to 5 years, and its productive capacity is 4 to 5 tons of zinc per calendar day or up to 90 kg per square metre of heated area (as against about 15 kg per square metre of heated area in the horizontal retort).

Table 41 compares the performance and economics of both the horizontal and vertical retort processes.

Table 41
**Comparative Performance and Economics of the
 Horizontal and Vertical Retort Processes**
 (per ton of zinc)

Variable	Horizontal retort	Vertical retort
Heating and reduction fuel (coal), tons	2.22-2.39	1.54-1.71
Labour, man-hours	29-43	7.7-12.5
Zinc recovery, per cent	86.4-87.8	90-94

The zinc vapour leaving the retort is condensed to liquid zinc in condensers. They are made of firebrick and have inside partitions to extend the path covered by the zinc vapours. Owing to this arrangement coupled with a nearly constant gas composition and high zinc vapour concentration, up to 85 per cent zinc is condensed to liquid metal. The remaining uncondensed zinc vapour and entrained blue powder passing out of the condenser with the residual gases are scrubbed out by water sprays and the zinc is recovered as a fine dust. The scrubbed carbon monoxide gas is pumped back into the retort setting—a feature which saves about 20 per cent fuel.

91. Zinc Distillation in Electric Furnaces

Though more efficient than the horizontal retort process, the vertical retort process is disadvantageous in that heat has to be transmitted through the retort walls. The heating of the charge from within would raise distillation temperature and, consequently, zinc recovery while the walls would remain relatively cold. This idea has been materialised in what is known as the electrothermic process.

This process uses tall electrothermic furnaces 12 to 14 m high, made of firebrick. The charge consists of agglomerated zinc-bearing materials and coke. Current is supplied by graphite electrodes, the electrode spacing, top to bottom, being 8 to 10 metres. The numerous electric arcs striking between the lumps of coke heat the charge to an average temperature of 1200°C. The spent residue is discharged continuously, and it contains 15 to 16 per cent Zn.

The recovery into slab zinc is 90 per cent, and energy consumption is anywhere between 2500 and 2800 kWh/ton.

Zinc distillation is also carried out in arc-resistance furnaces which may measure 4 m by 8 m in plan and up to 2.5 m in height. Current is supplied through three graphite electrodes passed into the furnace through the arch. In operation, the furnace carries a bath of molten iron covered by a blanket of molten slag. The ends of the electrodes are dipped in the slag, and the temperature of the bath is maintained at 1300-1350°. The charge consisting of zinc oxides, coal and flux is introduced through ports in the arch. Zinc recovery in arc furnaces is up to 95 per cent with a power consumption of about 3300 kWh/ton.

In both types of electric furnaces, the charge is preheated to 850-900°C with the carbon monoxide recovered from the zinc condensers. Without preheating, energy consumption would have been much greater.

Zinc distillation in electric furnaces has necessitated the use of what is known as the splash condenser having a deep zinc bath. To speed up condensation, the molten zinc bath in the condenser is held at a definite temperature by water-cooled coils. A motor-driven graphite or steel impeller dips into the molten zinc and fills the condenser chamber with a rain of coarse drops of molten zinc on which the zinc vapour condenses with practically no blue powder formed in the process.

As any type of distilled zinc, the one produced by electric distillation requires refining to remove iron, lead and cadmium.

92. The Production of Zinc in a Blast Furnace

After many years' investigation, zinc is now being produced on a commercial scale from water-jacketed blast furnaces at the Avonmouth Works, Britain.

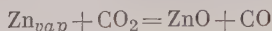
From the behaviour of zinc in the blast-furnace smelting of lead, it can be realised what formidable problems have had to be tackled by that smeltery.

The blast furnace uses air preheated to between 550 and 750°C in order to reduce the zinc percentage passing into the slag. The air blast is supplied through water-cooled tuyeres. The higher temperature in the furnace reduces the zinc content in the slag to 3 per cent.

The column of charge is maintained high so as to catch the dust which would otherwise interfere with the condensation of the zinc vapours.

The furnace gases containing CO, CO₂ and zinc vapours are partly burned on their way from the furnace to the splash condenser. The

resultant temperature rise prevents zinc from being oxidised according to the reaction (see the equilibrium diagram in Fig. 142)



The gas entering the condenser at about 900°C contains up to 13 per cent carbon dioxide, but the zinc vapour is not oxidised due to the low rate of reaction and the high rate of condensation of the zinc vapour. Zinc vapour condensation is speeded up by the molten lead

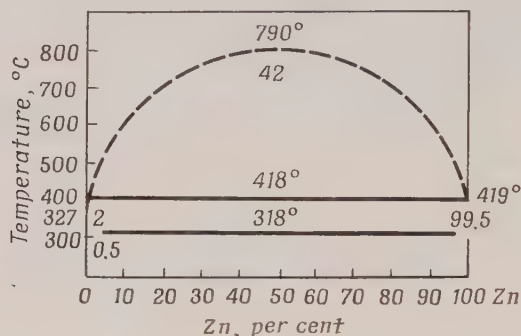


Fig. 144. Constitution diagram of the system Zn-Pb

splashed about in the condenser which uses water-cooled coils and a motor-driven impeller. Its rate may be described by the following equation:

$$v = K (p_1 - p_2)$$

where v = rate of condensation;

K = constant dependent on the conditions of condensation;

p_1 = zinc vapour pressure in the gas;

p_2 = equilibrium vapour pressure above the molten bath.

Referring to the equation, the rate of condensation increases as the value of p_2 decreases.

On condensing, the zinc dissolves in the molten lead, and the pressure of its vapour above the alloy may be expressed by Raoult's Law:

$$p_2 = p_{\text{Zn}} \frac{n}{n + N}$$

where p_{Zn} = vapour pressure above pure zinc;

n = mole fraction of zinc in the zinc-lead alloy;

N = mole fraction of lead in the same alloy.

The value of p_2 will decrease in comparison with p_{Zn} as the zinc content of the alloy decreases.

The hot lead containing the condensed zinc is continuously pumped from the condenser and through a water-cooled launder. As the lead cools, the excess zinc separates from it according to the diagram in Fig. 144. It is collected in a separator bath as a pool on top of the lead flowing below. The overflow zinc assays about 1.5 per cent Pb. The underflow lead impoverished of zinc to 2.3 per cent is pumped from under the zinc in the separator bath back into the condenser. About 400 tons of hot lead has to be circulated through the condenser in order to condense one ton of zinc. Using zinc concentrates with 20 to 38 per cent Zn and 16 to 27 per cent Pb, zinc recovery by this process is up to 90.8 per cent, and lead recovery, 94 per cent.

The daily capacity of this blast furnace with an area of 6.4 sq m at the tuyeres is about 40 tons of zinc.

93. The Refining of Slab Zinc

Table 42 summarises the requirements for commercial grades of zinc as specified by the U.S.S.R. State Standard 3640-47.

Table 42

Commercial Grades of Zinc

Designation	Min. zinc, per cent	Max. impurities, per cent							
		Pb	Fe	Cd	Cu	As	Sb	Sn	total
II B	99.99	0.005	0.003	0.002	0.001	—	—	—	0.01
II 0	99.96	0.015	0.010	0.010	0.001	—	—	—	0.04
II 1	99.94	0.024	0.015	0.014	0.002	—	—	—	0.06
II 2	99.9	0.05	0.04	0.02	0.002	—	—	—	0.1
II 3	98.7	1.0	0.07	0.2	0.005	0.01	0.02	0.002	1.3
II 4	97.5	2.0	0.15	0.2	0.05	0.01	0.02	0.05	2.5

While hydrometallurgical zinc meets the requirements for Grades II 0, II 1 and II 2, distilled zinc often fails to approach those for II 3. The demand for Grade II 4 is very limited, and so all distilled zinc has to be refined.

Two principal methods are available for refining zinc: liquation and redistillation. Liquation is based on differences in solubility and specific gravity, especially on cooling. It is mainly used to remove lead and iron. Redistillation, or fractional distillation, utilises the difference in boiling points of zinc and its impurities.

It may be used to upgrade a very contaminated spelter to zinc of high purity (Grade II0). Simultaneously it removes lead and cadmium as very concentrated products suitable for the subsequent production of these two metals.

While electrolytic refining of zinc is possible, it is seldom used because of the prohibitively high consumption of energy. In fact, the refined zinc would be more expensive than that produced hydro-metallurgically.

Refining by Liquation. The extent to which lead and iron can be removed from crude zinc by liquation depends on the equilibrium in the systems Zn-Pb and Zn-Fe (see the equilibrium diagrams in

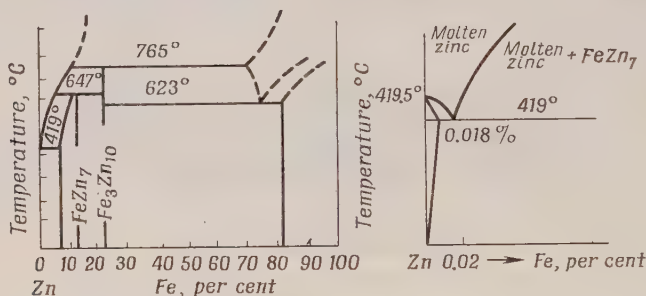


Fig. 145. Constitution diagram of the system Zn-Fe

Figs. 144 and 145). Referring to Fig. 144, there is a region of limited solubility. At 418°C, the molten metal would separate into three strata. The lighter top stratum would contain 0.5 per cent Pb and 99.5 per cent Zn, and the heavier bottom stratum 98 per cent Pb and 2 per cent Zn. Practically, the limit to which the molten metal can be cooled for liquation must be somewhat above the eutectic point, or between 420 and 430°C, as otherwise it would solidify. The bottom stratum carries about 97 per cent Pb and 3 per cent Zn, while the top zinc stratum contains 0.7 to 0.8 per cent Pb.

The iron content of crude zinc rarely exceeds 0.2 to 0.3 per cent, and the dross forming during liquation answers the chemical formula FeZn_7 (Fig. 145). The crystals of FeZn_7 sink in molten lead. Theoretically, it seems possible to remove all iron in this way. Actually, however, its content can only be reduced to 0.02 or 0.03 per cent owing to the low rate of crystal settling.

Liquation makes it possible to combine lead and iron elimination in a single step. Crude zinc is melted in a reverberatory furnace of up to 150 tons capacity, fitted with grates. The molten bath is held in a quiescent state at 420 to 450°C for 24 to 48 hours until it

fully separates. The bottom stratum collects lead. Sandwiched between the top and bottom strata is the mushy layer of iron-zinc alloy mixture of solution and FeZn_7 crystals. About one-third of the top zinc layer is drawn or dipped off through an opening in the rear end of the furnace at regular intervals, and fresh crude zinc is added. The liquated zinc is then cast into moulds, and the iron-zinc dross and lead are removed periodically as they accumulate. The iron-zinc alloy is drawn with perforated dippers; its crystals usually entrain some molten zinc and contain not over 5 or 6 per cent iron. The dross is re-treated with a distillation charge. The molten lead containing 93 to 94 per cent Pb and 4 to 6 per cent Zn is drawn by means of a pipe with teeth at an obliquely cut end, which is introduced into the furnace through the emptying slot. The lead is sent to lead smelteries for use in the recovery of the precious metals.

Refining by Redistillation. Redistillation or fractional distillation utilises the difference in vapour pressures and boiling points of zinc and its impurities. The boiling points (in degrees C) of some metals follow:

Cadmium	767
Zinc	906
Lead	1750
Copper	2360
Iron	3235

As has been noted elsewhere (see Table 40), at 1000°C the pressure of lead vapour is about 1 mm Hg, while that of copper and iron vapours is negligibly low (10^{-4} and 10^{-6} mm Hg, respectively).

Putting it another way, zinc can be easily separated from iron and copper by evaporating it; there is some difficulty, however, in separating zinc from lead by this method.

The vapours produced by the evaporation of a solution are always higher in the more volatile component which in our case is cadmium. In Fig. 146 the lower curve shows the boiling point of a Zn-Cd alloy as a function of its analysis, and the upper curve relates the composition of vapours to the composition of the boiling liquid.

Let alloy *a* containing about 5 per cent Cd be boiling. Then, according to the diagram, its vapour will contain 12 per cent Cd (point *b*). Having cooled the vapour of composition *b'* down to 870°C so that the system is shifted towards a two-phase region, we shall obtain a liquid *a'* containing some 30 per cent Cd. Another cooling cycle to 830°C will produce a liquid *a''* containing 25 per cent Cd, and a vapour *b''* carrying 63 per cent Cd. Following this procedure of consecutive evaporation and condensation, it is possible to separate an alloy into pure components. Zinc refining by fractional

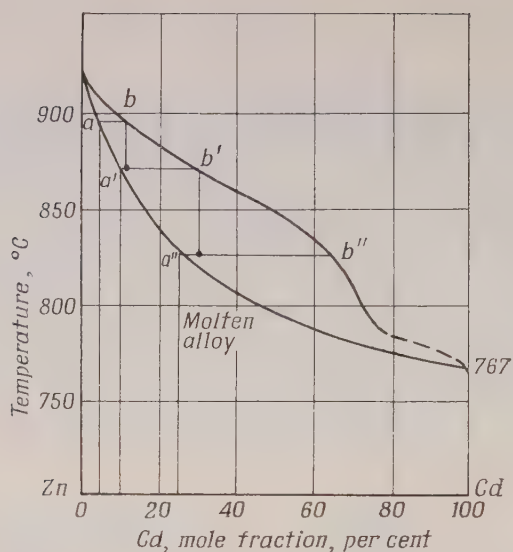


Fig. 146. Equilibrium for boiling Zn-Cd alloys and the progress of redistillation (after Chizhikov and Sevryukov)

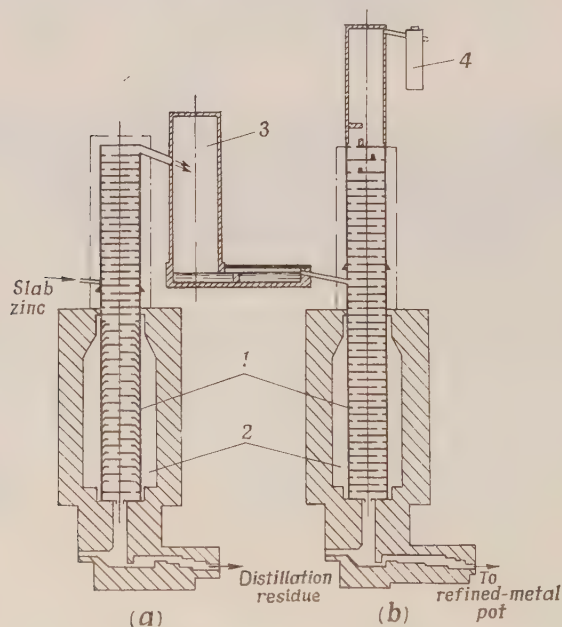


Fig. 147. Apparatus for refining zinc by fractional distillation:

(a) lead column; (b) cadmium column; 1—vaporiser; 2—combustion chambers; 3—condenser; 4—cadmium canister

distillation is exactly this process of consecutive evaporations and condensations which however take place simultaneously in a fractional distillation apparatus.

The apparatus (Fig. 147) consists of a furnace which melts crude zinc to give a continuous flow of molten metal into a lead column (at *a* in Fig. 147). In the lead column the crude zinc is purified of

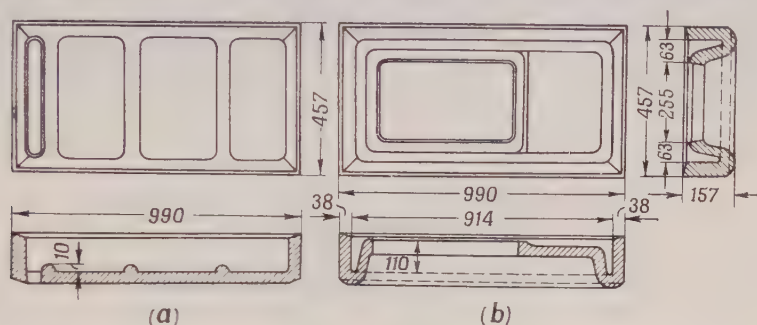


Fig. 148. Bonded silicon refractory trays for rectifying columns:
(a) flat-bottomed; (b) with uplift floor

lead and iron. The resulting zinc vapours are cooled in the condenser (3) to produce a liquid metal which is partially distilled and rectified in the cadmium column (at *b* in Fig. 147). The cadmium vapours are discharged into the cadmium canister (4). The rectified molten zinc is collected in the refined-metal pot.

Each rectifying column consists of superposed trays made of a bonded silicon carbide refractory. Their shape and dimensions are shown in Fig. 148, while Fig. 149 shows an assembled column. The trays are so assembled that an opening through the floor near one end of each tray is alternated to give a baffled flow for descending liquid metal and ascending vapours. Around the opening is a raised rib for holding a shallow layer of molten zinc.

The column is composed of two types of trays: boiler (with an uplifted floor) and refluxing (with a flat bottom). The section containing boiler trays is within the fired chamber (2 in Fig. 147) and supports the section of refluxing trays above the fired chamber. The boiler trays have a V-V section, with the V legs forming a continuous trough all the way round the periphery to hold the crude molten zinc in contact with a large proportion of the column wall heated from the outside.

In operation, the molten feed zinc is continuously poured onto the refluxing tray (1*R*) so that it overflows onto the boiler trays (1*B*, 2*B* and 3*B*) in succession. The boiler trays are heated from the outside by burning producer gas, and the molten zinc on them is boiling

continuously. As the molten zinc descends, its temperature increases because its boiling point rises as more cadmium is vaporised. In rising up the column, the metal vapours come in contact with a shower of descending molten metal. Some of the vapours condense on the refluxing trays to overflow down again on the boiler trays. The refluxing trays are heated solely by the heat of condensation; the liquid metal on them is likewise boiling continuously; the temperature of the refluxing trays progressively decreases towards the top as the cadmium content in them increases. Ascending zinc

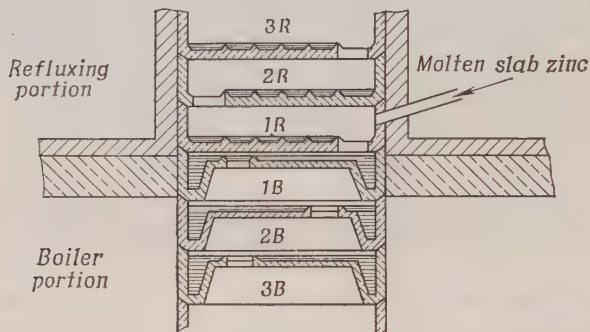


Fig. 149. Sectional view of a rectifying column

vapours continue to be purified until they reach the top tray and cross over into the lead-column condenser.

Both the boiler and refluxing sections of each column have 20 trays, and so only about four-fifths of the zinc can be vaporised, the remaining metal passing into the residue together with the impurities. The residue carrying 6 to 8 per cent Pb is channelled into a liquating pot from which the zinc layer is returned to the lead column together with new feed zinc. More zinc may be vaporised with a larger number of trays, which is not, however, an attractive proposition economically.

The pure zinc drawn from the bottom tray of the cadmium column contains over 99.99 per cent Zn and meets the requirements for Grade IIB.

Cadmium recovery by fractional distillation is often over 90 per cent—an obvious advantage, for cadmium is nearly 15 times as expensive as zinc. The resulting cadmium is obtained as dust in the cadmium-column condenser which also collects a mixture of cadmium and zinc oxides containing up to 40 per cent Cd.

The daily capacity of fractional distillation apparatus varies with the size of trays. The figure for an apparatus consisting of two lead columns and one cadmium column which use trays measuring 500 mm by 1000 mm is about 20 tons of pure zinc per calendar day. Zinc recovery is 95 to 96 per cent. Some 4 or 5 per cent passes into liquated products, and about 0.6 to 1 per cent are irrecoverable losses. Fuel consumption (in terms of fuel equivalent) is about 40 per cent of the zinc treated.

Fractional distillation was introduced on a commercial scale in the Soviet Union in 1936. It has eliminated one of the gravest drawbacks of zinc pyrometallurgy—contaminated metal.

94. Recovery of Scrap Zinc

Many of the by-products of zinc production contain much zinc, lead, copper, cadmium, gold and silver. Their re-treatment improves overall zinc recovery from ores and makes it possible to utilise associated metals.

The main by-products of zinc production are retort residues and leaching residues. Their analysis is summarised in Table 43.

Table 43

Approximate Analysis of Retort and Leaching Residues

Residue	Content, per cent						
	Zn	Pb	Cu	Fe	C	SiO ₂	CaO
From retorts	6-11	1-15	max. 4	13-24	19-20	12-22	max. 3
From leaching	15-20	1-14	max. 4	23-32	—	2-4	—

Fuming in a rotary kiln (the Waelz process). Retorts and leaching residues as well as lean ores which are difficult to beneficiate can be treated for the recovery of their zinc and lead contents by fuming.

The kiln employed for the purpose is described in Sec. 116 dealing with the metallurgy of aluminium. The kiln used in zinc production measures anywhere between 30 and 45 m in length, and from 2 to 3.5 m in diameter. It is installed with a pitch of 3 to 5 degrees of arc and rotates at 0.75 to 1.5 rpm. The fuel may be pulverised coal, fuel oil or gas. The hottest zone with a temperature of the order of 1200°C is within 3 to 7 metres of the discharge end, and the flue gases leave the furnace at 500 to 600°C.

The charge consists of the secondaries to be re-treated, limestone, and coke breeze with particles not over 10 to 20 mm. The limestone and excess coke breeze prevent the charge from fusing and keep it in a loose state. The charge travels through the kiln during 2 or 3 hours. In some cases, no fuel is required in addition to the coke breeze in the charge.

On burning, the coke breeze produces a reducing atmosphere in the kiln. The carbon monoxide reduces the metal oxides, and the zinc, cadmium and lead are vaporised. Their vapours rise above the charge and are oxidised by the oxygen and carbon dioxide of the kiln gas. These oxidised materials form a fume consisting of very small solid particles which travel through the kiln suspended in the gas stream. Some components of the charge, such as lead and cadmium oxides and sulphides, may be vaporised directly.

The fumes are collected in electrostatic precipitators or bag-houses. Fumes low in the metal sought are returned to the charge. Fumes high in cadmium are re-treated for the recovery of cadmium, and those low in cadmium for the recovery of zinc. The analyses of fumes are summarised in Table 44.

Table 44

**Approximate Analyses of Fumes Obtained from
Retort and Leaching Residues**
(per cent)

Grade	Zn	Pb	Cd	Fe	Cu	SiO ₂
1st	66.3	4.6	0.4	1.4	0.2	0.5
2nd	40.4	8.4	0.3	11.0	0.5	6.5

The incandescent material discharged from the kiln consists of a porous, semifused mass, called the Waelz slag which is resmelted in blast furnaces for the recovery of lead bullion and copper-lead matte collecting also gold and silver. The matte is further re-treated to remove its copper, lead, gold and silver contents.

Reduction smelting in a blast furnace. This method is mainly applied to retort residues, because leaching residues would have to be briquetted before smelting, which is obviously a disadvantage. Fuel consumption is relatively low, as the retort residue always contains some carbon. The values of the residue are reduced and oxidised to form fumes or vaporised directly, and the fumes are carried by the gas stream into fume-catching equipment.

95. Extraction of Other Metals from Zinc Concentrates

Among all the associates of zinc, the principal one is cadmium which usually assays about 0.2 per cent.

Cadmium is mainly used in the manufacture of alkali storage batteries. Some quantity of this metal is used for plating to produce decorative and anti-corrosion coatings on other metals, in anti-friction alloys, and in dentistry. Small additions of cadmium to copper reduce its electrical conductivity insignificantly but improve its strength appreciably.

The abundance of cadmium in the lithosphere is estimated at 5^{-5} to 10^{-5} per cent. Cadmium ores proper are not known to exist. For the most part cadmium is present in complex ores (almost invariably associated with zinc). In the differential flotation of complex ores the cadmium is distributed between the lead and zinc concentrates, and so some cadmium is also recovered as a by-product of lead.

In sintering lead concentrates volatile cadmium oxide and sulphide are collected in flue dust. Little cadmium is present in the flue dust obtained in the roasting of zinc concentrates for hydrometallurgy, because the temperature used in the process is relatively low.

The leaching of zinc calcines distributes their cadmium content roughly equally between the solution and the residue. From the solution it is then withdrawn into a copper-cadmium residue. From zinc residues the cadmium is fumed by oxidising-reducing roasting.

Where zinc concentrates are treated pyrometallurgically, some cadmium is fumed, and the fume is caught during the second roasting. In distillation, the cadmium of the sinter passes into the crude zinc and, though to a lesser degree, to blue powder; yet the cadmium percentage in the blue powder is greater. From crude zinc the cadmium is recovered by fractional distillation.

To sum up, the main sources of cadmium supply are the flue dust from the sintering and roasting of lead and zinc concentrates; condensed fume and blue powder; copper-zinc residue; and the dust from the cadmium condenser in fractional distillation.

The recovery of cadmium from all of the above sources is a complicated process and is usually done at electrolytic zinc plants.

In order to reduce the weight of the materials to be shipped, the source material is given primary concentration at the place of production. To this end, flue dust, fumes and blue powder are leached with sulphuric acid. The lead sulphate, silicic acid and other insolubles remain in the residue, while the zinc and cadmium pass into solution as sulphates. From the resulting solution the cadmium is precipitated with zinc dust; the cadmium sponge from

this operation is then compressed and distilled and redistilled in cadmium smelteries.

Fig. 150 shows a flow-sheet for the production of cadmium from the copper-cadmium residue. The residue is roasted to oxidise the copper and cadmium. The calcine is then leached with sulphuric acid. The solution is next purified of the copper with zinc dust. After the cemented copper has passed into the residue, the solution is again treated with zinc dust to precipitate the cadmium sponge.

The primary cadmium sponge, either from an outside supplier or obtained locally from the copper-cadmium residue, and redistillation dust are dissolved in sulphuric acid. The solution is thoroughly purified of iron, arsenic, antimony, copper and other impurities and is then electrolysed. The cathode cadmium is melted under a blanket of an alkali in order to protect it from oxidation and to purify it additionally. In the case of a low-grade cadmium sponge, it is dissolved in sulphuric acid and precipitated with zinc dust several times.

Sometimes, zinc concentrates may also carry thallium, indium and germanium which may be recovered alongside with cadmium.

In zinc hydrometallurgy, the roasting of zinc concentrates volatilises up to 85 per cent of the thallium, mainly as Tl_2O . The subsequent leaching of the calcines and flue dust causes the bulk of the thallium (to the extent of 75 to 90 per cent) to pass into solution as Tl_2SO_4 . All in all, thallium removal from concentrates into solution amounts to 65 to 75 per cent. On the other hand, the bulk of the indium and germanium passes from concentrates into the zinc residue during iron purification as hydrates and basic salts.

When the solution is purified of copper and cadmium, as much as 50 to 80 per cent of the thallium is precipitated to be recovered as a by-product of cadmium. From a solution of cadmium sulphate (Fig. 150) the nearly insoluble $TlCl$ can be precipitated by an addition of sodium chloride.

Sometimes the leaching of zinc concentrates or fumes may cause a considerable quantity of indium to pass into solution. In such cases, indium is collected in the copper-cadmium residue from which it is recovered during the recovery of cadmium.

As has been noted elsewhere, zinc residues which carry the bulk of the indium and germanium contained in the original concentrate are treated by the Waelz process. As a result, 70 to 90 per cent of the indium and about 40 per cent of the germanium pass into fumes together with the remaining cadmium and thallium. The volatile form of indium probably is In_2O and of germanium, GeS .

In some cases, the Waelz fumes are considerably enriched with indium or germanium. In such a case, the fumes are leached with sulphuric acid in two stages. The first, or neutral, leach produces

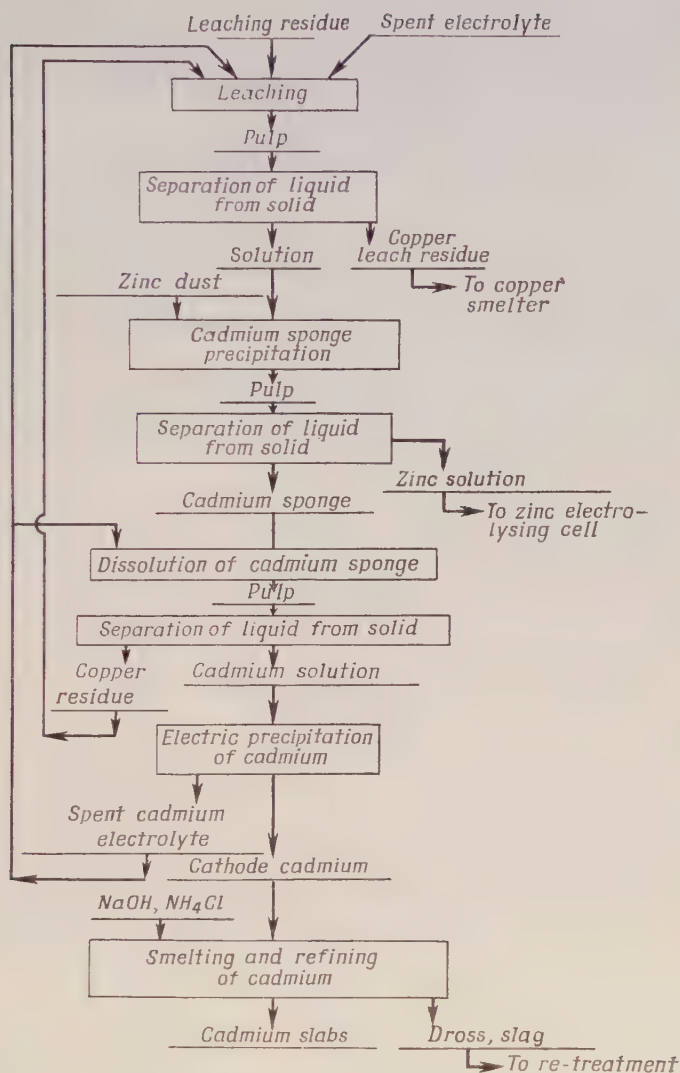


Fig. 150. Scheme for cadmium recovery from copper cadmium leaching residue

a solution carrying zinc, cadmium and thallium which is treated separately. The second, acid, leach dissolves either the germanium or the indium. From a sulphate solution, germanium may be thrown out by atomised zinc; it will pass into solution together with copper, but preferentially to cadmium and thallium, as can be seen from the electrochemical series quoted below:

Cu	Ge*	In	Tl	Cd
+0.34 V	-0.13 V	-0.32 V	-0.34 V	-0.40 V

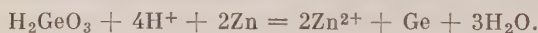
Indium from such solutions may be advantageously precipitated together with the basic iron sulphate, while keeping the pH of the solution down to 3.5 or 4.

In zinc distillation, thallium forms a fume which is caught during roasting.

Indium is reduced and vaporised together with zinc and is collected in crude zinc and, to some degree, in blue powder. In zinc redistillation, indium passes into the zinc-bearing lead which is treated for the production of lead.

In the case of distillation processes, germanium remains in the retort residue which is then treated by the Waelz fuming process as described elsewhere.

* Germanium is precipitated by zinc according to the reaction



Part Four

THE METALLURGY OF THE PRECIOUS METALS

Chapter XI

THE METALLURGY OF GOLD

96. General

Gold has a face-centred cubic crystal structure, melts at 1063°C and boils at 2950°C . As measured at normal temperature, its specific gravity is 19.26.

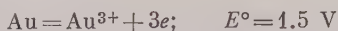
Gold has a somewhat greater hardness than has copper (a Brinell hardness of 45). On the other hand, it is extremely ductile, being easily drawable to fine wire and rolled or beaten to foil or leaf with a thickness of less than one micron. Here is a comparison of the foil obtainable from several metals:

Metal	Au	Ag	Al	Pt	Cu
Foil thickness, micron	0.08	0.2	0.2	0.25	0.34

The thermal and electrical conductivity of gold is about 25 per cent lower than that of copper.

Gold forms two series of compounds, with valencies of 1 and 3. Divalent gold compounds are known but they are unstable. Ions of Au^{3+} are yellow in colour and possess strongly oxidising properties.

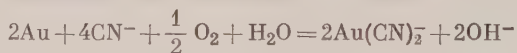
Gold owes its insolubility even in hot strong acids to its high electrode potential:



It may be caused to pass into solution only by strong oxidising agents such as aqua regia.

Gold does not oxidise in air or oxygen. Au_2O_3 has a positive change of standard free energy; gold oxide can only be obtained indirectly, and it is unstable.

Hydrocyanic acid and the alkali cyanides dissolve gold in the presence of atmospheric air. This property is utilised to cause gold to pass into aqueous solutions:



For centuries gold has been used as the monetary standard owing to its permanency and rarity in comparison with other metals. Considerable quantities of gold are used for jewelry and in the dental field. Some gold is used in instrument-making, laboratory work and in medicines.

97. Sources of Gold

The bulk of the gold occurs in nature in native form. Large grains of gold (over 0.1 mm in size) are found relatively seldom. Occasionally, gold is found in nuggets several kilograms in weight. Grains of gold widely differ in form (Fig. 151).

Native gold is by no means a pure metal. It contains up to 20 per cent silver, the platinum-group metals, copper, iron, mercury, lead, bismuth and some other metals. Natural alloys of gold making up gold grains differ materially from man-made alloys of the same analysis both in structure and component distribution.

Gold also occurs in the form of tellurides and selenides. As a rule, gold-bearing ores are earthy materials with gold grains, tellurides or selenides disseminated in them. Sometimes, the disseminated grains may be so fine as to be beyond the resolving power of the microscope, in which cases one may speak of a condition very close to solid solution.

The gold content of ores varies widely, the most common figure being 5 to 15 grams per ton. For surface placers worked by means of dredgers, hydraulic giants or monitors and excavators the economically attractive gold content today is about 1 gram per ton.

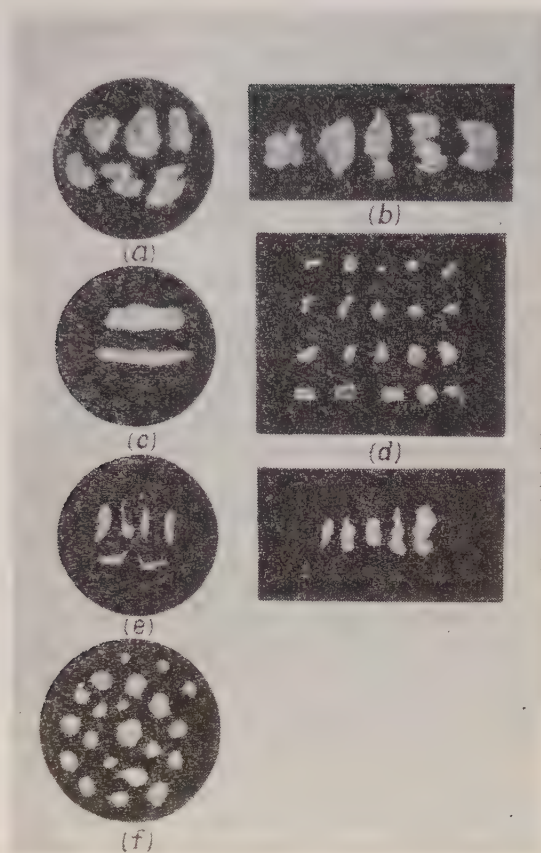


Fig. 151. Gold grains (or colours), after Shabarin:

(a), (b) concretions, magnification 12 \times ; (c) bars, magnification 12 \times ; (d) flakes, magnification 45 \times ; (e), (f) oblong concretions, magnification 45 \times ; (g) spheroids, magnification 45 \times .

In the case of vein or reef gold, where other metals occur but rarely, the economically attractive limit of gold content is 3 to 5 grams per ton, depending on the depth of occurrence.

98. Methods of Gold Recovery

The choice of a particular method for treating gold ores depends above all on whether or not a given ore contains any other values and in what proportion. Where the ore carries commercially attractive amounts of copper or lead in addition to gold, the copper and lead contents are recovered by the pyrometallurgical processes already described, and the gold is obtained by refining the crude copper and lead. This is the simplest and cheapest method of gold recovery.

In the case of placer gold or gold ores carrying no other values, resort is made to gravity concentration, which is based on the difference in the specific gravities of gold grains (17 or 18) and the gangue (2.6 to 5). At gold mines, this is done on jigs, concentration tables and other machines (described later). Sometimes concentration separates heavy minerals, such as sulphides, in which gold is included as minute particles.

In many instances, concentration is part of some other gold-recovery system in which it plays the role of a preparatory stage. True, in some cases it would be possible to recover the gold as "gold sand", but the losses would be too high. This is why gravity concentration produces only a concentrate which is treated by other methods.

Another method of gold recovery is known as amalgamation. For its effect it depends on the property of gold to form an alloy with mercury, known as amalgam, even at room temperature during a momentary contact.

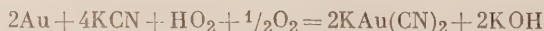
Amalgamation is carried out in a plant which provides for intimate contact between the water pulp of ground ore and mercury. After the amalgam has been separated from the pulp, the excess Hg is removed by squeezing the amalgam through chamois or canvas bags. The amalgam, squeezed quite dry and hard, contains 20 to 50 per cent bullion.

The squeezed amalgam is finally retorted to distil the mercury (mercury boils at 357°C) which is then condensed in condensers. The gold is left as the retort metal which is melted to separate the silver content and refined of impurities.

Amalgamation is a simple and cheap process. It is efficient, however, when applied to the coarse free gold whose surface is not covered by other materials handicapping contact with mercury. In modern practice amalgamation is almost exclusively used as an auxiliary treatment for the recovery of the bulk of the coarse Au clean on the surface.

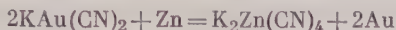
In the latter half of the 19th century what is known today as cyanidation was first introduced. The scientific basis for the new process had been laid by Bagration of Russia, who discovered the solubility of gold, silver and copper in cyanides of alkali and alkali-earth metals and put forward a theory of the process.

Cyanidation, also known as the cyanide process, extracts gold and silver from ores by means of the solvent action of an alkaline or alkali-earth cyanide solution on these metals with the formation of double cyanide groups:



The necessary oxygen is taken from the atmosphere. The gangue does not react with cyanides and can be filtered out after leaching.

From the leach the gold is precipitated by zinc dust:



When the ore has been ground fine, the cyanide process can extract very fine gold. While with amalgamation the recovery rarely exceeds 85 per cent, the figure for cyanidation is 95 to 97 per cent. The reasons why gravity concentration and amalgamation are still in use are their relative simplicity, cheapness, and ability to recover coarse gold.

Cyanidation is a typical hydrometallurgical process. Other hydrometallurgical processes for gold recovery are also known. Way back in the 18th century Lomonosov suggested that gold could be covered by chlorination and leaching with aqua regia. Being less attractive economically, these processes have not found appreciable commercial application. In recent years, new solvents have been developed for gold recovery, such as thiourea, but their use is still in the experimental stage.

The progress made in flotation has made it applicable to the metallurgy of gold. Both native gold and sulphides are floatable down to very fine sizes of gold and silver grains. Flotation gold concentrates always contain sulphides or arsenides of other metals, and the choice of the further treatment depends on which metals are present. Where the gold concentrate carries copper and lead, it seems advantageous to use pyrometallurgy and to recover the gold from the crude metals by any of the known processes. Where the gold concentrate is free from other values, cyanidation seems to be the only alternative.

The above processes and methods may be combined in a variety of ways to suit a given ore and prevailing conditions.

99. Gravity Concentration

Gravity concentration of gold-bearing ores uses jigs, concentrating tables, sluices and hydraulic traps. They are run in closed circuit with mills and classifiers or placed at the discharge of a classifier after the ore has been ground to the requisite grain size.

Sluicing. A sluice is an inclined table over which the feed pulp is allowed to flow down in a thin stream. The behaviour of the solid particles depends on their size, specific gravity, friction against the surface of the sluice and the velocity of the stream.

The velocity of the pulp varies across the stream, being the highest at the surface and approaching zero at the bottom. Therefore, the solid particles in the stream tend to stratify (according to grain size and specific gravity), the heavy gold sinking to the bottom and

the lighter gangue being carried away by the stream. Large light-weight particles are driven down the slope by the stream of pulp.

The slope of the sluice, the depth of the stream, the velocity of the pulp, and the material of the sluice surface can all be so chosen as to obtain a concentrate of the desired fineness and specific gravity. This task is facilitated by preliminary classification.

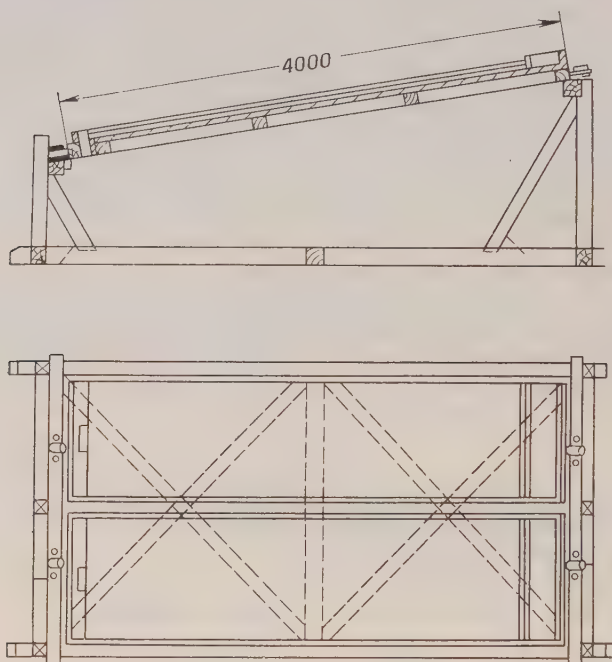


Fig. 152. Double-deck sluice with corduroy covering and rotating decks

The surface of the sluice may be covered with corduroy (coarse thick ribbed cotton stuff), velveteen with broad and widely spaced ribs, ribbed rubber matting, cloth, coarse carpets, felt, tarpaulin, canvas, burlap, etc.

Sluice are fitted with riffles which have three chief functions: (a) to retard the material moving over them and give it a chance to settle; (b) to form pockets to retain gold which settles on them; and (c) to form eddies which roughly classify the material in the riffle spaces.

The same is true of the pile fabric with which the sluices are covered. As the pile of the fabric covering increases, the recovery of the gold into the concentrate also increases, but the resulting concentrate becomes lower in gold due to the lodgement of some gangue.

With time, the riffles and corduroy covering collect much gold, and the classifying action of the sluice becomes less efficient. For this reason, the sluices are given regular clean-ups.

To facilitate clean-ups, double-deck sluices are often used (Fig. 152) in which the decks can be rotated on axes. For a clean-up, one deck is tilted through 60° , and the concentrate is washed down by a jet of water, while the other deck remains in operation.

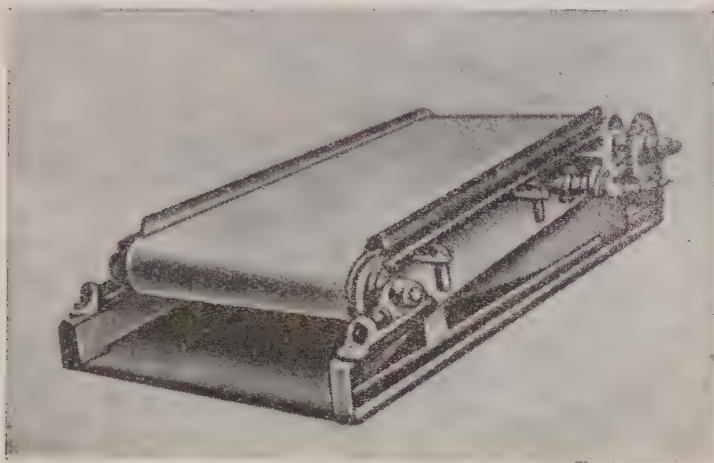


Fig. 153. Belt sluice

The capacity of sluices is expressed in terms of ore treated per square metre of deck area per calendar day. For coarse gold it is 20 tons, and for fine gold and sulphides 1.5 to 10 tons.

Higher daily outputs are obtained with belt sluices mainly used to re-treat concentrates, to treat sulphide ores and other materials with a high concentrate yield. A belt sluice (Fig. 153) is an endless rubber belt stretched between two drums one of which is power-driven (by a motor) and the other is idle. The belt has a covering of pile fabric and moves against the current of the feed pulp. At the raised end the concentrate is continuously discharged by rakes and a rotating cylindrical brush. The normal rate of belt travel is 0.75 to 1.5 m/min. Higher rates increase output, but the resulting concentrate is lower in gold.

Of late, automatic multi-deck sluices have come into use. Some of them may have five decks set one above another on a common bedframe (Fig. 154). Operation and clean-ups alternate at intervals of 4 or 5 minutes. The pulp is fed by a distributor to the raised ends

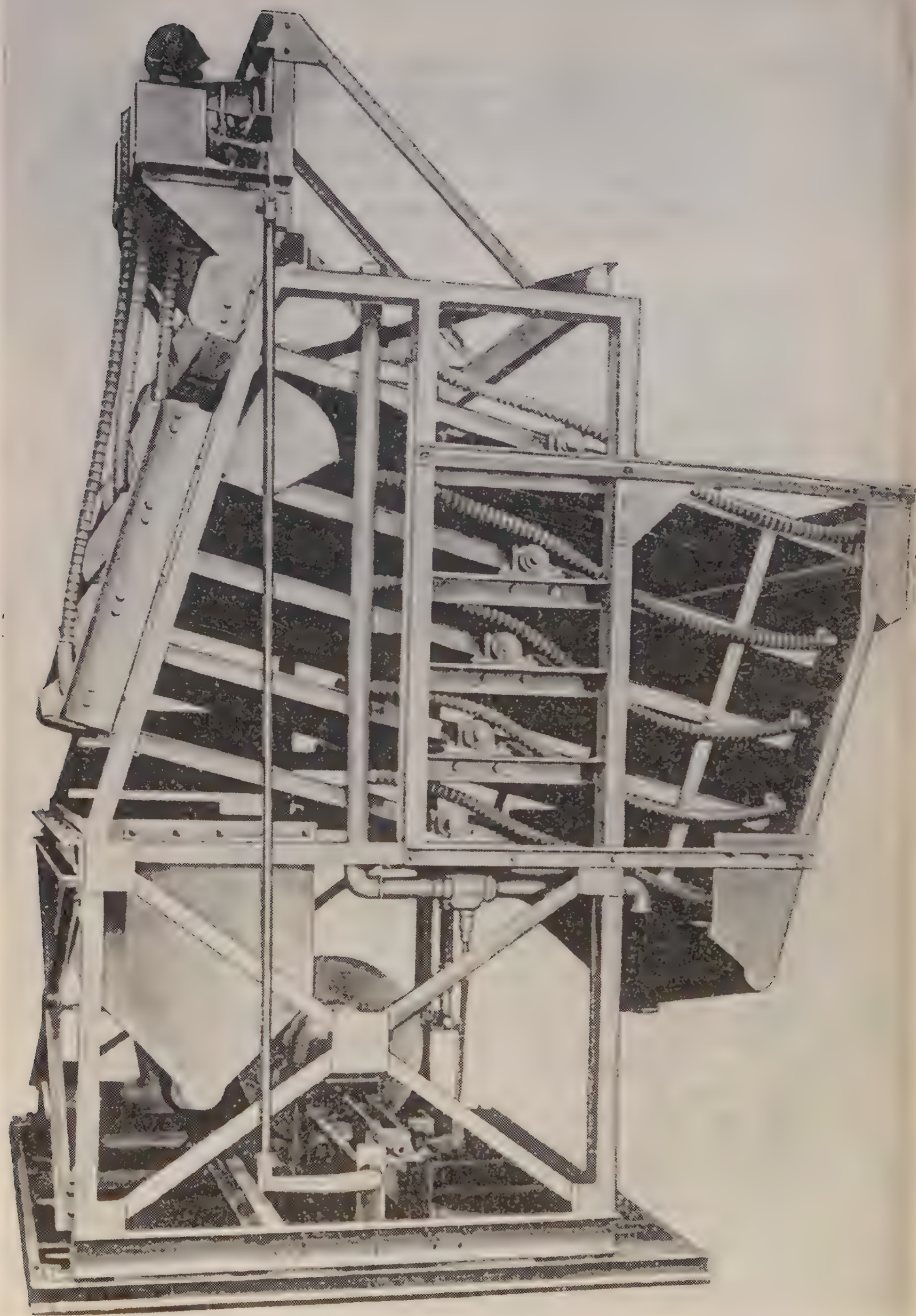


Fig. 154. Automatic five-deck sluice

of all the decks and flows down the pile-fabric covering. For a clean-up, the pulp is stopped, the lowered ends of the decks are raised and the raised ends lowered, and water is turned on to wash down the concentrate from the raised decks.

A five-deck sluice with a total surface area of 16 sq m can handle 6 to 10 tons of ore an hour, although it is relatively compact in size, measuring $2320 \times 2660 \times 3370$ mm.

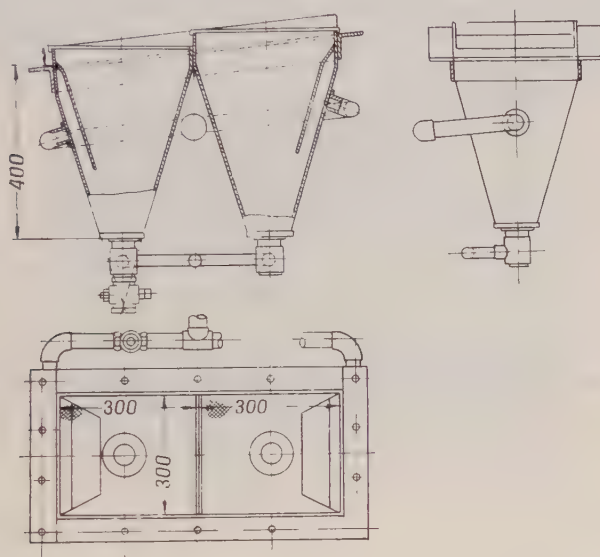


Fig. 155. Hydraulic trap

The feed pulp for sluices with pile-fabric coverings contains 30 to 80 per cent particles in the 0.07 mm class. The liquid-to-solid ratio of the pulp usually is 3-6 to 1 (sometimes 8-10 to 1). Gold recovery ranges between 30 and 80 per cent, and concentrate yield is 0.1 to 5 per cent of the ore weight.

Hydraulic traps which also serve to remove heavy particles from the feed pulp are simple in construction and efficient enough in service. A trap is a series of cones or pyramids connected by troughs (Fig. 155). Hydraulic traps are run in closed circuit with crushing or milling plant or placed at the discharge of classifiers. For better removal of oversize, water is fed into hydraulic traps either at the top and bottom, or only at the bottom. The advantages of hydraulic traps over sluices are compact size and reduced water consumption, their gold recovery is however lower.

Gold-bearing ores are jigged on diaphragm-type and pulsator jigs described in Sec. 8.

Jigs are usually run in closed circuit with crushing and milling equipment. The bed used in the jigs may be of cast-iron shot, crushed magnetite and other similar materials with particles measuring from 6 to 13 mm across.

The concentration ratio depends on many factors the principal among which are the composition and fineness of the ore. For plunger-type jigs it ranges between 1 : 25 and 1 : 250, while for pulsator jigs the figure may be as high as 1 : 2000 and even 1 : 10,000. The gold content of jigged concentrates varies within broad limits—from 50 to 500 g/ton or even more.

100. Amalgamation

According to Plaksin, the system Au-Hg has three chemical compounds (AuHg_2 , Au_2Hg and Au_3Hg) and solid solution carrying 16.7 per cent Hg. Their melting points are above 100°C . The solubility of gold in mercury at ordinary temperature is about 0.2 per cent.

When it comes in contact with gold, mercury wets and penetrates it to form solid solution and then the three compounds. The resulting amalgam is a mechanical mixture of solid particles and liquid mercury. The solid particles of the amalgam are non-uniform in composition; their surface coating consists of solid solution and the chemical compounds, while the core may remain unaffected (in the case of large gold grains). Longer contact with mercury renders them more uniform, and they approach chemical compounds in composition throughout their mass.

The rate of amalgamation depends on how efficiently mercury wets the gold grains and on their surface area. Mercury containing 0.2 per cent Au or about 0.05 per cent non-precious metals will wet gold better than pure mercury owing to the fact that the impurities reduce its surface tension. Any further increase in impurities sharply reduces the wetting action of mercury because the impurities are oxidised and the oxides form a film around mercury droplets.

Amalgamation may be handicapped by soluble copper salts which may be present in the feed pulp due to the oxidation of natural sulphides. Small additions of lime to the feed pulp will precipitate the copper as copper hydroxide, which is usually done in commercial amalgamation.

Native gold is sometimes difficult to amalgamate not only because it is an alloy but also on account that the gold grains are covered with oxides, sulphides and other compounds. The film may be

abraded mechanically in crushing and grinding equipment. The requisite fineness depends on the size of the gold grains and other features of the ore under treatment and is established by trial and error.

Comminution and amalgamation may be carried out simultaneously in the same equipment, in which case the process is termed inside amalgamation. If done after comminution, it is called outside amalgamation. Current practice uses both.

In inside amalgamation, the freshly scoured gold grains have no chance to come into long contact with an oxidising medium.

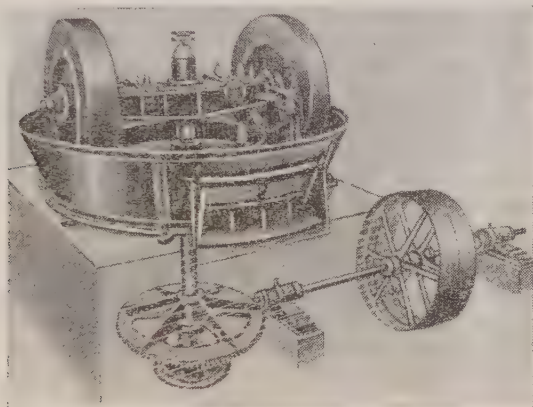


Fig. 156. Muller pan

A drawback of inside amalgamation is that the mercury undergoes flouring and sickening: during ore comminution it forms a mass of microscopic globules, like flour, which are coated with a film of oxides of other base metals, lubricating oil, or fine particles of ore and refuse to coalesce. Floured and sickened mercury is difficult to separate from the ore, and much of it is lost, carrying off some gold with it.

Inside amalgamation is applicable to concentrates obtained by gravity concentration, and also to other gold-bearing materials.

The usual grinding equipment—ball and rod mills—are unsuitable for inside amalgamation as they “flour” the mercury heavily. Usually the ore is comminuted in muller pans (Fig. 156). For its operation a muller pan depends on the crushing and attrition of ore lumps by heavy mullers rolling on a hard ring-shaped slab.

The muller pan is an annular trough armoured with hard steel plate on the bottom. The vertical shaft passing through the centre

of the pan rotates at 13 to 16 rpm. The top end of the shaft carries a spider with bearings for the muller axles.

The mullers are of cast iron and have renewable steel rims. Each muller is made fast to its axle whose end fits into the bearing of the spider. Modern muller pans usually have three mullers.

The ore is fed mechanically after it has been reduced in size to 20 to 50 mm. Simultaneously, water is poured to obtain a liquid-to-solid ratio of 8-12 to 1. Mercury is fed at intervals of $1\frac{1}{2}$ to 2 hours in small increments in the proportion of 5 or 6 grams of Hg per gram of gold recovered. Once a day or in two days the muller pan is stopped for cleaning up the amalgam.

The amount of ore reduction in muller pans depends on the grade of the ore being treated; ores containing coarse gold require less reduction than those carrying fine gold. Usually, the final product has a fineness from minus 0.2 to minus 0.6 mm.

The outer wall of the pan has an opening covered with a net and partly closed by an iron baffle. Reduction can be adjusted by varying the height of the baffle and the rate of feed of the ore.

Output depends on the size of the pan, the weight and speed of the mullers, the initial and final fineness of the ore and its hardness. Excessive speed may result in heavy flouring of the mercury.

For a pan 1.8 m in diameter and a muller weighing 3.6 tons, the daily output of a muller pan will be 45 to 65 tons of ore.

The inside amalgamation of gravity concentrates and other materials high in gold and available in small amounts is carried out in barrels (barrel amalgamation). Barrels (Fig. 157) come in especially useful when the ore has to be finely ground.

The shell of an amalgamation barrel is in cast iron; the ends have bosses for trunnions with which the barrel rests on bearings.

The barrel is loaded with the concentrate, steel balls, mercury, some lime and water through an opening covered with a hermetically sealed lid. The duration of barrel amalgamation is anywhere from 2 to 10 hours. At the end of that period, the barrel is stopped, the lid removed, and the contents emptied into a trap and sluice to separate the amalgam. In emptying, the balls are retained within the barrel by the metal net in the opening.

Outside amalgamation uses apron plates and amalgamators. Mechanical amalgamators have proved of low efficiency and are now used in very few cases, preference being given to apron plates.

Apron plates (Fig. 158) are wide, shallow, sloping troughs of annealed copper 3 to 5 mm thick, mounted on heavy wooden tables. The copper plates are rubbed with mercury; sometimes they are silver-plated prior to mercury application. Apron plates are usually 5 to 6 metres long, 1 to 2.5 metres wide and have a slope of 8 to 10 per cent.

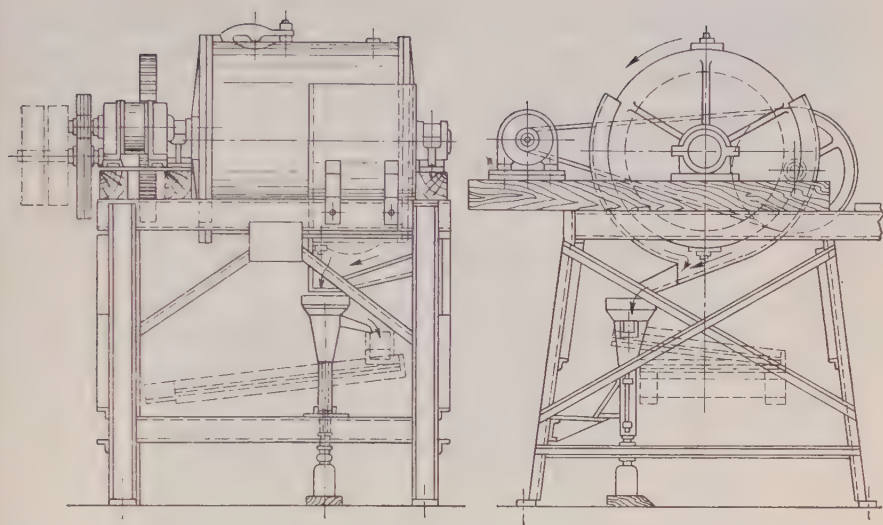


Fig. 157. Amalgamation barrel with a trap and sluice

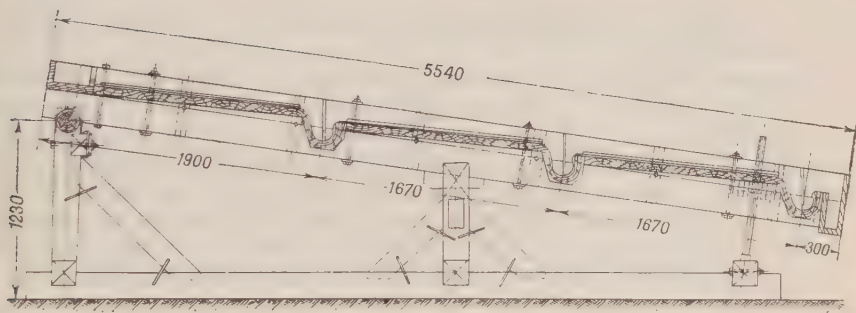


Fig. 158. Amalgamation apron plates

The feed pulp is charged into a distribution box at the upper end of the plates whence it is allowed to flow down the amalgamated surface. The gold grains in the lower layer of the stream come in contact with the mercury and stick to the plates. The coarse gold and amalgam are trapped by transverse grooves spaced 1.5 to 1.8 metres apart. Furthermore, at the foot of the plates there is a mercury trap which consists of a simple transverse trough with a riffle or a hydraulic seal (Fig. 159).

Once a day the plates are stopped, the amalgam removed with rubber or leather scrapers, and the copper plates again dressed with mercury.

Apron plates usually follow inside amalgamation in order to recover additional gold grains, mercury and amalgam from tails.

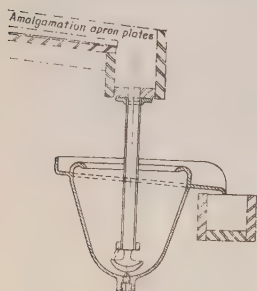


Fig. 159. Mercury trap at the foot of amalgamation apron plates

Also they may be employed for gold recovery prior to cyanidation or flotation.

The capacity of apron plates is expressed in terms of the surface area required to handle one ton of ore per calendar day. In the case of pulp coming from mullers, the figure is 0.3 to 0.5 sq m, while for gold recovery from the ores to be flotated or cyanided 0.1 to 0.2 sq m will suffice.

The amalgam from mullers, amalgamation barrels and apron plates widely differs in composition and density. A dense amalgam is difficult to separate from entrained ore particles; therefore, dense amalgams are usually mixed with thinner grades or diluted with mercury.

The first step in the subsequent treatment of amalgam is to wash it repeatedly with hot water in cast-iron or porcelain pans. Metallic iron from mill balls or lining is removed by a magnet. The washed amalgam has a mirror-bright surface. It is then squeezed in chamois or canvas bags in hand or power presses. The mercury strained out in squeezing the amalgam is returned to the process, and the squeezed dry amalgam is finally retorted for distilling off the mercury.

Distillation uses a brick furnace setting and cast-iron bottle-shaped retorts with detachable covers (Fig. 160). The amalgam is charged into retorts on iron trays covered with nets or perforated iron plates. The mercury vapours escaping from the retorts are condensed and returned to the process.

At the beginning of distillation the temperature should be maintained at 300 to 400°C, as higher temperature may cause the mercury

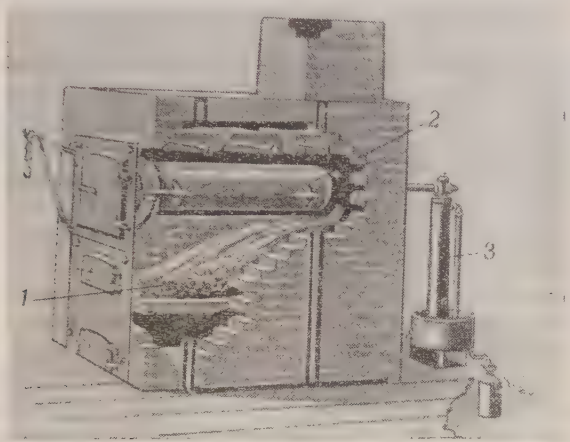


Fig. 160. Retort and brickwork setting for distilling off amalgam:

1—firebox; 2—retort; 3—mercury condenser

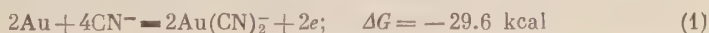
to boil violently and spatter. Then the temperature should be gradually raised to 750 or 800°C so as to complete the distillation in 3 to 6 hours.

The retort metal, or mill bullion, contains 750 to 900 parts of gold in a thousand. The mercury content does not exceed 0.1 per cent.

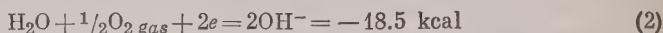
The mill bullion is then melted in graphite crucibles, using sodium carbonate, borax and nitre as fluxes and oxidisers, and cast into bars 6 to 8 kg in weight. During melting, the base metals are partly oxidised and pass off into slag. The bars of gold are then sent for refining.

101. Cyanidation

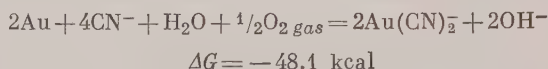
The solubility of gold in cyanides of alkali or alkali-earth metals, discovered by Bagration (Russia), is due to the formation of double cyanide groups according to the equation



This reaction necessitates the oxidation of the gold. In an alkaline medium, such as cyanides, this purpose can be served by atmospheric oxygen:



Adding together equations (1) and (2) gives an overall reaction and the corresponding change in the standard free energy:



The solubility of oxygen in diluted cyanide solutions is close to its solubility in pure water which, according to the Henry Law, is proportional to the partial pressure of O_2 in the gaseous phase and decreases with rising temperature. Under normal conditions, the maximum solubility of oxygen in cyanide solutions is 7 or 8 mg/litre. The oxygen spent to dissolve gold should be continuously replenished from the atmosphere. Passing into solution, the atmospheric oxygen has to go through two diffusion layers: one at the interface between the atmosphere and the solution and the other at the interface between the solution and the gold. According to Plaksin and co-workers, the rate of diffusion is the lowest near the surface of the gold and it governs the rate of cyanidation. This is the reason why an increase in cyanide concentration fails to speed up the extraction of the gold from the ore. Usual practice is to employ solutions containing but 0.03 to 0.15 per cent NaCN. On the other hand, cyanidation can be speeded up by agitation, although it pays to increase the intensity of agitation only as long as the concentrations are equalised at a rate lower than that of diffusion at the interfaces. Past that point, an increase in agitation only involves higher power consumption without affecting the rate of cyanidation.

Heated solutions speed up the diffusion of oxygen but reduce its solubility. Commercially, solutions are seldom heated (only when their temperature drops to below 8 or 10°C), since this involves considerable fuel consumption. Furthermore, while speeding up cyanidation, the heating entails losses of cyanide on unproductive reactions.

Still another method to speed up cyanidation is to conduct it under air pressure or with pure oxygen. In both cases, more oxygen will dissolve in the solution and its rate of diffusion will increase. This method is however used on a limited scale yet.

Of the numerous cyanides, the best solvents of gold are cyanides of alkali and alkali-earth metals. The activity of CN ions in their aqueous solutions is sufficiently high while the materials are stable and relatively cheap to produce.

Originally, cyanidation used potassium cyanide as a solvent. Later on, preference was given to the cheaper sodium cyanide. More recently, calcium cyanide has come into use.

Calcium cyanide is manufactured in the form of a melt with other salts (known as "black" cyanide). Although it contains impurities and has to be used in amounts twice as great as sodium cyanide, black cyanide has come into wide use currently.

Cyanidation should be conducted in an alkaline medium; the presence of free acid reduces the concentration of CN ions and produces gaseous HCN.

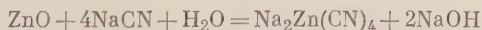
Stoichiometrically, 0.49 g of NaCN would suffice to dissolve 1 gram of gold. Practically, 20 to 100 times as much sodium is required. Much cyanide is lost due to its decomposition by atmospheric carbonic acid, interaction with associated minerals and mechanical causes.

All those substances found in ores and tailings which decompose or render useless some of the cyanide are appropriately called cyanicides.

Cyanide solutions easily dissolve native copper, malachite, azurite, chalcocite and bornite, and less eagerly chalcopyrite and chrysocolla. The presence of copper minerals in gold ore may increase cyanide losses to a point where it may prove unprofitable to recover the gold at all. As a way out, coppery gold ores should be treated with heavily diluted cyanide solutions, as the dissolution of copper minerals in them is slowed down more than that of gold.

Iron minerals do not react directly with cyanides, but ferric hydrate, iron sulphate and basic sulphate fix CN ions into $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_2$, etc. The presence of iron minerals slows down cyanidation mainly owing to the fact that some oxygen is spent to oxidise the sulphides in the feed pulp. The adverse effect of iron sulphides on cyanidation can be moderated by roasting and aerating the pulp prior to cyanidation so as to oxidise the iron to ferrous hydrate. Furthermore, the pulp may contain 2 to 5 kg per ton of finely divided iron from crushing and grinding plant; this iron will also slow down cyanidation by consuming some oxygen and forming $\text{Fe}(\text{CN})_6^{4-}$.

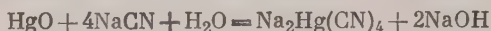
Zinc minerals rarely occur in gold-bearing ores. Zinc sulphides do not practically react with cyanides, while zinc oxides and carbonates pass into solution readily:



The above reaction explains why in the presence of zinc sulphide it may prove disadvantageous to roast or aerate the pulp preparatory to cyanidation.

The mercury that is left in the ore after amalgamation does not react with cyanides. Still, if the ore has been exposed to air, the

mercury may be oxidised, and cyanide consumption may be increased due to the following reaction:



Minerals of arsenic and antimony do not react with cyanides but are dissolved in alkalis to form thio- and oxysalts which are readily oxidised in the feed pulp, thereby "stealing" some oxygen. Arsenical ores may be roasted prior to cyanidation so as to volatilise arsenic trioxide.

Lead sulphide has no appreciable effect on cyanidation; its salts like PbSO_4 and PbCO_3 , however, do slow down the dissolution of gold appreciably.

After gold precipitation, cyanide solutions are strengthened with fresh cyanide and are again used to dissolve gold from ores. Continuous re-use of solutions ultimately results in the accumulation of impurities, mainly soluble complex salts of Zn and Cu, and the solution becomes "fatigued". The presence of 0.03 per cent Cu and 0.05 per cent Zn may reduce the rate of gold dissolution by as much as 5 to 10 per cent, although cyanide concentration may remain unchanged. The opinion has been advanced that fatigue is due to the adsorption of impurities by gold grains and the resulting reduction in the area of contact between the gold and solution.

The cyanide process uses two techniques of solution treatment: percolation and agitation. In the former case, the material is charged into vats or tanks with filter bottoms and is given a succession of percolation leaches with cyanide solution while the material remains stationary. In the latter case, the material is treated by cyanide solution in agitation tanks while being held in suspension due to the difference in the velocity of the solid particles and liquid.

After preparing an ore, the pulp may be classified into coarse and fine products (sands and slimes). Sands are treated by percolation, and slimes by agitation. Sometimes all the ore may be ground fine and treated by the all-slime technique, which is true of ores containing fine gold. Conversely, all the ore may be ground coarse and then it will be treated by the all-sand technique, which is true of ores containing coarse gold.

Nowadays, ores containing coarse gold are relatively rare. Furthermore, coarse gold can be successfully extracted by gravity concentration and amalgamation. So, cyanidation is mostly applied to fine-gold ores which require a good deal of size reduction. As a result, percolation treatment is losing ever more ground to agitation treatment or, rather, the all-slime technique.

Percolation vats or tanks are built of wood or steel plate. The latter are sturdier but more expensive than wooden tanks; their

use is therefore warranted at plants handling large quantities of ore or in cyaniding rich ores.

A wooden tank (Fig. 161) is assembled of pine or larch staves 60 to 100 mm thick held together by iron hoops. Usually, percolation tanks are 5 to 10 metres in diameter, 2.3 to 3.5 metres in height

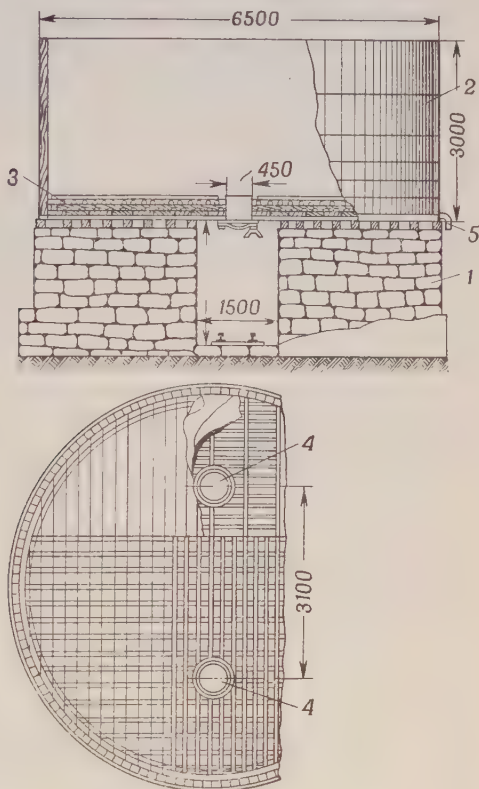


Fig. 161. Percolation vat for the cyanide process:

1—foundation; 2—vat; 3—filter bottom; 4—discharge openings; 5—solution port

and 50 to 300 tons of ore in capacity. The bottom is made of boards as thick as the walls and fits into a chime on the inside surface of the tank.

Steel tanks are often made rectangular for ease of charging and discharging; they hold 500 to 800 tons of ore.

The filter-bottom consists of a grating made of wooden rectangular bars with orifices in the supporting frame, overlaid by bast matting and filter cloth, and over this is spread a grating to protect the filter against damage when the tank is charged or discharged. Below the filter-bottom there are solution charge and discharge gates.

Tanks may be charged with either dry or wet sands. In the former case, the sands are delivered by cars riding a rail track above the tank, or by belt, scraper-chain and pneumatic conveyers, or grab-bucket cranes, etc.

The wet pulp comes from the classifiers and is evenly distributed by some automatic device or a portable hose.

After charging, cyanide solution is run into the tank to cover the charge. Practice varies as to admitting the solution at top or bottom of the tank. The former is more often although better results are obtained with the latter: the material is uniformly permeable and the slime does not clog the filter; but this practice does not aerate the pulp well.

The complete leaching of gold requires several intermittent floodings and drainings of the charge using different solutions each time. The first and strongest solution for a quartz ore at one plant contained 0.12 per cent NaCN, the second 0.06 per cent and the third 0.03 per cent, after which the final flooding used clear water. Vacuum drainage is used at some plants in dewatering the charge after final washing.

In a typical case, percolation leaching will be completed in 4 to 10 days, depending on ore grade, tank size, and use of power charging and discharging.

Although percolation leaching is simple and cheap, gold extraction with it seldom exceeds 85 to 90 per cent, the average being 60 to 70 per cent, which is a poor showing at the present state of the art.

That is the reason why it is giving way to agitation treatment.

The requirements that a successful agitation tank should meet are provision of facilities for continuously stirring the thickened slimes, different velocities of solids and liquid in the tank, and the possibility to aerate the charge sufficiently.

Agitation of the slime may be done by mechanical stirrers, compressed air, or, more efficiently, by a combination of both. Hence the most common type of tank is one using both a mechanical stirrer and air. Combination-type tanks or agitators may be with a central airlift and a peripheral airlift.

Agitators using a central airlift are built of wood or iron. Their dimensions usually are: diameter, 1.8 to 9 metres; height, 3 to 7 metres; effective capacity, 12 to 350 cu m.

A central-lift agitator (Fig. 162) consists of a hollow vertical shaft revolving at 2.5 to 4 rpm. At the bottom end of the shaft is attached a spider with plows like those of the Dorr thickener. The plows draw the settled slime towards the centre beneath an opening in the hollow shaft. The central pipe descending through the shaft supplies compressed air which causes the pulp to rise up the shaft as a suspension. At the tank top the pulp flows down two slightly

inclined launders mounted on the shaft. The launders have perforated bottoms through which the pulp flows back into the tank. The joint action of the air jet and the flow of the pulp through the holes in the launders improves the aeration of the material.

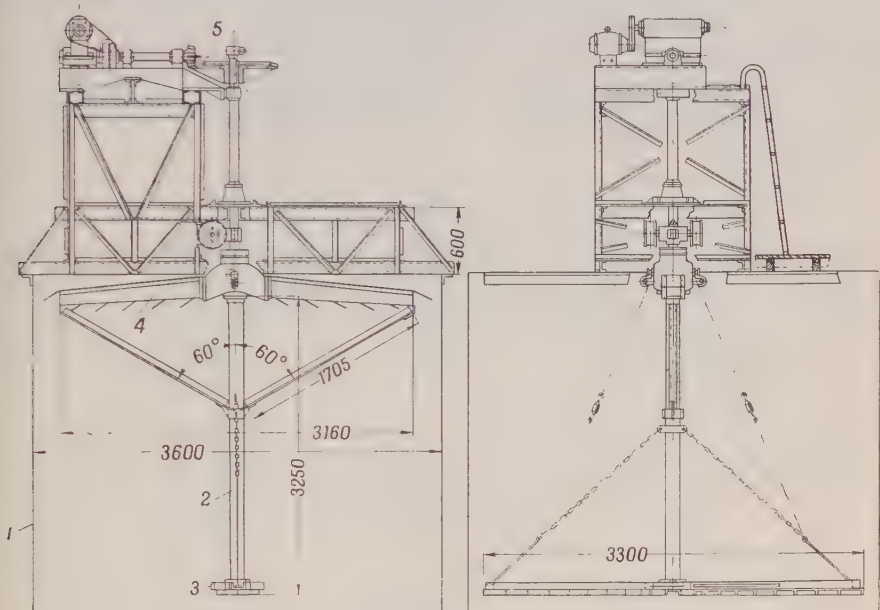


Fig. 162. Central-lift agitator:

1—tank; 2—hollow shaft; 3—spider and plows; 4—launders; 5—shaft drive

Of late, the trend has been towards using several airlifts mounted on the periphery of the tank. In this case, the pulp is made to circulate more vigorously and better aeration is attained. Now agitators with multiple peripheral airlifts are in use at many plants.

Edge-lift agitators (Fig. 163) are available in capacities from 6 to 58 cu m and are made in steel plate or, more seldom, from wood.

Such an agitator has a central vertical iron pipe 50 to 70 cm in diameter which terminates within some distance of the bottom. The pipe has several open ports and carries the shaft of a propeller stirrer in the inside. The steel impeller beneath the bottom end of the pipe rotates at 130 to 200 rpm.

Above the impeller there is a steel disk which protects the impeller from damage, should the settling ore fall down during an accidental shut-down.

The agitator has four airlift pipes bent at the top and led into the central pipe. Each airlift pipe carries a tube supplying compressed air. The impeller draws in the pulp from the central pipe and throws it towards the tank walls. As a result, the pulp is sucked into

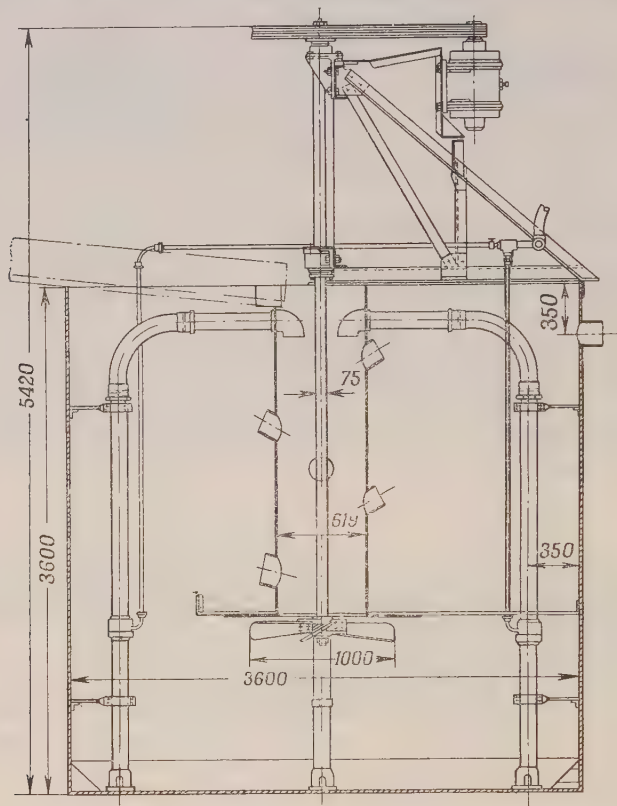


Fig. 163. Edge-lift agitator

the central pipe through the open ports. In addition, some pulp is fed into the central pipe by the airlifts. Similar agitators use paddle stirrers, but their handling capacity is lower, although they consume less power.

Slime treatment may use either continuous or batch agitation. In the latter case, the pulp is fed into and drawn from the tank continuously. This improves gold extraction, as the larger pieces which are more difficult for the airlift to raise, stay in the tank longer.

Furthermore, leaching may be conducted in a series of tanks with the pulp flowing through them consecutively for as long a time as may be necessary for the desired gold extraction to be attained. Series treatment (sometimes also called continuous treatment) saves the time occupied by charging and discharging. At the present time, it has been adopted at most gold factories.

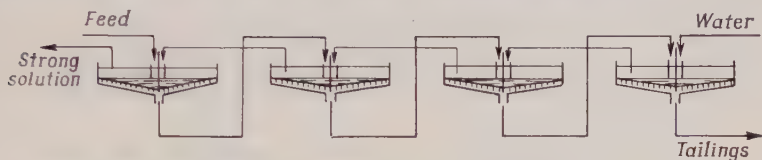


Fig. 164. Diagram of continuous counter-current decantation

The next step in the cyanide process is the separation of the dissolved metals. Where percolation leaching is employed, the tank simultaneously serves as a filter. In the case of agitation treatment, however, the solution has to be thickened and filtered in order to separate tailings, and the filter cake is washed.

A very simple and cheap method for separating the bulk of the solution is by thickening. The thickened product is then filtered in drum, disk or any other filters. The cake is thoroughly washed to remove the traces of the gold-bearing solution, and the wash water is returned to the leaching stage.

In some cases, a more attractive proposition is to use what is known as continuous counter-current decantation. In simple decantation the material is allowed to settle, the clear liquid is decanted off, the vessel refilled with clear water to the previous level, the residue stirred, and decantation repeated. The whole cycle is thus performed several times until the desired extraction of gold from the solution is attained. Where half the solution is decanted off each time, the first decantate will contain 50 per cent of the dissolved gold, the second 25 per cent, the third 12.5 per cent, etc. Five decantations will remove $50 + 25 + 12.5 + 6.25 + 3.12 = 96.87$ per cent of the dissolved gold into the clear product.

A serious drawback of simple decantation is that every next decantate grows increasingly diluted, and their total volume rapidly increases. This may be avoided by using the barren or low-grade solutions or washes for the make-up for a succeeding decantation, say the fifth decantate for the fourth decantation, the fourth decantate for the third decantation, etc. Such a process is called counter-current decantation. It can be carried out continuously in a series of thickeners (Fig. 164).

In continuous counter-current decantation, the solids with a small portion of liquid are pumped successively from the bottom portion

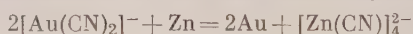
of one thickener to the next, from the second to the third, etc., being finally discharged as tailings from the head thickeners. The bulk of the solution moves in a direction opposite to the course of the material and is gradually enriched. At each step a large volume of low-grade solution is mixed with a very small amount of high-grade solution, clear wash water being only added to the last thickener.

Continuous counter-current decantation is a simple and cheap method, but it requires large floor area. Where floor space is at a premium, multi-tray thickeners seem more attractive (Sec. 10).

102. Gold Precipitation from Cyanide Solutions

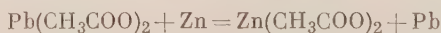
Gold from cyanide solutions can be precipitated by electrolysis and by cementation with other metals such as zinc or aluminium. Methods are also known in which gold is precipitated through adsorption by carbon or ion exchange resins, but they are still in a developmental stage.

The most commonly used method is zinc precipitation which may generally be presented by the following equation:

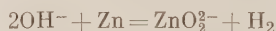


Plaksin and co-workers have shown that the rate of gold precipitation by zinc depends on the rate of diffusion of complex anions $[\text{Au}(\text{CN})_2]^-$ to the surface of the precipitant. When the latter is used in the form of shavings or fine dust, both anion diffusion and precipitation are speeded up.

Ions $\text{Au}(\text{CN})_2^-$ should not necessarily reach the surface of the precipitant—they may well discharge on the gold covering it, because gold is current-conducting. Similarly, the reaction can proceed on the surface of another metal in contact with the zinc, say lead which is added to the gold-bearing solution as lead nitrate and lead acetate to form on the zinc spongy lead with a well-developed surface:



The solutions from which the gold is precipitated always contain an excess of cyanide and some free alkali. Some zinc may react with the alkali to evolve hydrogen:



Thus, part of the zinc goes to precipitate the gold, and the balance produces hydrogen. The lead deposited on the zinc promotes gold precipitation while handicapping the discharge of the hydrogen ions, since hydrogen overvoltage on lead is greater than on gold or zinc.

Sodium zincate is soluble in water. If, however, the solution lacks free alkali, it will be hydrolysed to form an insoluble residue:



Where too little cyanide is present, the complex zinc salt decomposes:



The white residues of zinc hydroxide and cyanide settle on the zinc, thereby reducing the area of contact with the solution and slowing down gold precipitation. As a precaution, the pregnant solution should contain an excess of free cyanide (about 0.03 per cent) and alkali (0.01 to 0.12 per cent CaO).

Dissolved oxygen impairs the recovery of gold, because the latter is partially redissolved by the combined action of the cyanide and oxygen, the rate of redissolution increasing as more gold is precipitated due to an increase in the surface area of the gold precipitate. This can be prevented by de-aerating the solution in a vacuum prior to, and shutting off air during, precipitation.

Precipitation on zinc shavings, in open boxes, still used in some of the older mills, has given way to zinc-dust precipitation using de-aerated solutions.

De-aeration is done in an apparatus known as the dispersion tower or the vacuum receiver (Fig. 165). It is an iron cylinder 30 to 36 cu m in capacity, connected to a vacuum pump. The pregnant solution is poured through an opening in the cover and is allowed to flow into a checkerwork of wooden battens. Spreading over the battens, the solution readily gives up the dissolved gases. The de-aerated solution is collected in the conical bottom whence it is drained through a valve interlocked with the inlet valve so that the level in the vacuum receiver is maintained constant. The pressure within the receiver is 25 to 50 mm Hg.

A dust-precipitation unit operates continuously (Fig. 166). The clarified solution enters the vacuum receiver whose outlet port is connected to a centrifugal pump which is sealed and submerged in a tank holding cyanide solution as a precaution against air finding its way into the system. The pump transfers the de-aerated solution into a stirrer. A belt or any other feeder continuously feeds zinc dust into the stirrer the conical bottom of which is connected by a pipeline with a filter.

Both research and experience show that the rate of zinc-dust precipitation is the highest when the solution percolates through a layer of zinc dust in the filter and not during stirring-in. In other words, the short stay of the solution in the stirrer is of minor consequence, while the design of the filter is all-important to the opera-

tion of the zinc-dust precipitation installation. The most common types are filter-presses and vacuum leaf filters described earlier (Secs. 84, 85).

The vacuum leaf filter used for gold precipitation has frames, or leaves, radially arranged in a cylindrical pulp tank. Each leaf

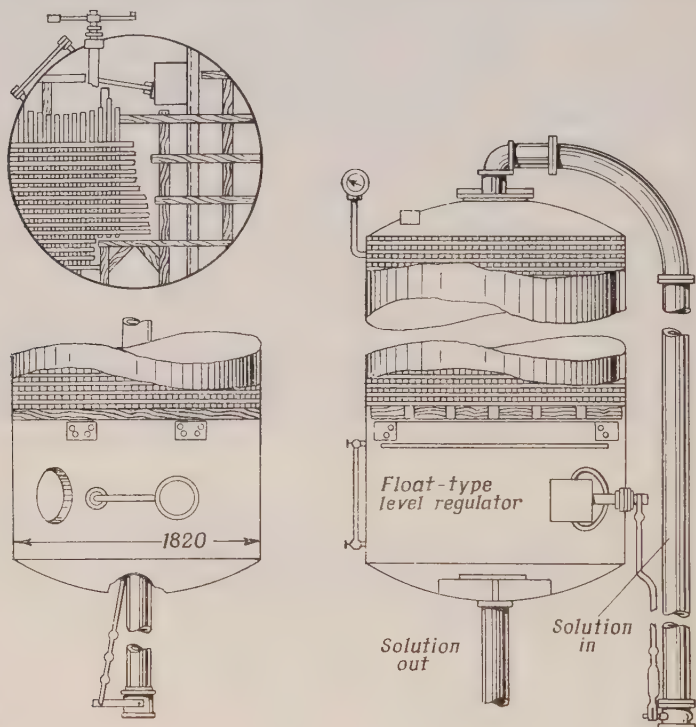


Fig. 165. Vacuum receiver for de-aeration of cyanide solutions

is connected to a common pipe header running all the way round the tank and in turn connected to a centrifugal pump. A central shaft carries a propeller stirrer beneath the leaves and a paddle wheel above the leaves to prevent the pulp from segregating during filtration.

The filter tank is open and the pulp is in contact with the atmosphere. Aeration of the pulp is however negligible owing to the high rate of filtration and insignificant stirring action which does not disturb the surface of the pulp.

With any filter design, the removal of the gold-bearing cake is done intermittently, and so for uninterrupted operation there

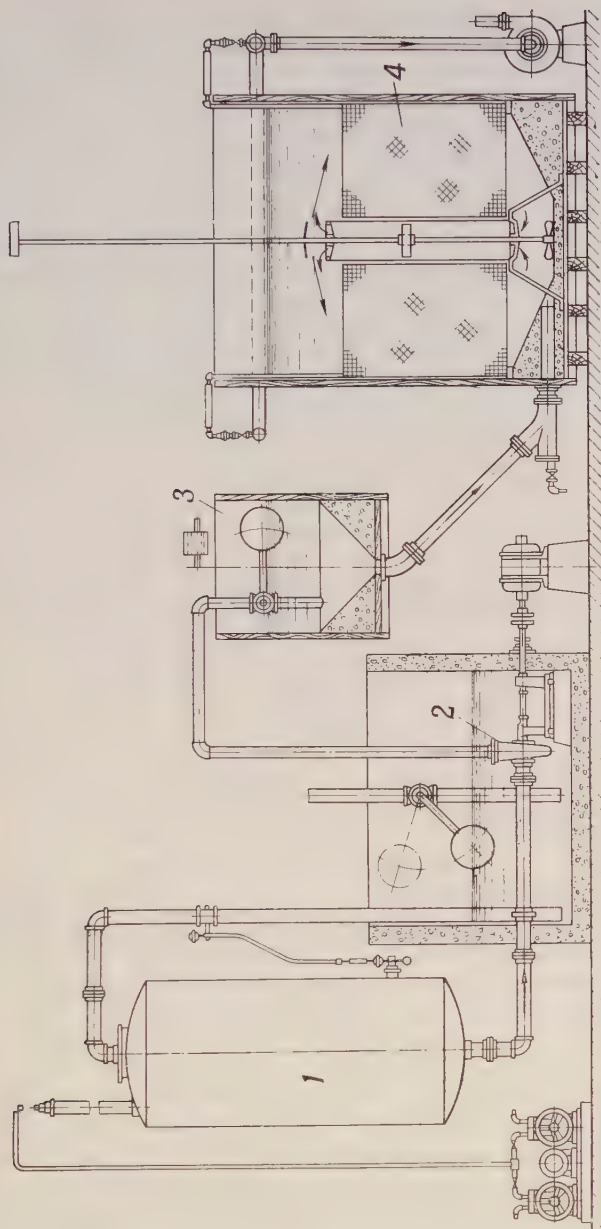


Fig. 166. Scheme for zinc-dust precipitation of gold:
 1 — vacuum receiver; 2 — pump submerged in cyanide solution; 3 — stirrer; 4 — leaf filter

should be two or three filters in service. Filter-presses are more convenient to operate and lose less cake in discharging.

The zinc-dust precipitate contains 20 to 50 per cent gold and silver (silver which is often included in gold grains responds to cyaniding much as gold does), excess zinc dust and impurities. The zinc and some of the impurities can be removed by heating and treating the precipitate with 40- or 45-per cent sulphuric acid in leaded tanks equipped with an exhaust ventilation. Exhaust ventilation is essential in order to vent out any HCN and AsCN that may form—both poisonous gases. The resulting pulp is then treated in filter-presses, the filtrate digested, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ crystallised out of it or the zinc directly precipitated with sodium carbonate. Both the $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and zinc oxides are by-products of the process.

In some cases treatment with sulphuric acid may be dispensed with, especially when the excess of zinc is negligible.

The gold-bearing precipitate, raw or acid-treated, is melted in crucibles or small reverberatories, adding sodium bicarbonate, borax, silica and, sometimes, fluorspar to the charge to oxidise and slag off the impurities. The molten charge is then poured into conical moulds. The slag is saved as it carries a good proportion of precious metals and is re-treated for their recovery. The metal is remelted and cast into bars weighing 6 to 8 kg each.

103. Typical Flow-sheets

The flow-sheets used in the gold industry commercially are diverse and complicated. As a rule, all of them combine several gold-extracting processes, depending on the nature, chemical and mineralogical composition of the ore available and the prevailing conditions.

The principal process is cyanidation. In commercial flow-sheets, however, it is usually preceded by amalgamation or gravity concentration and concentrate amalgamation which make it possible to extract coarse native gold at lower cost. A total of 60 to 70 per cent Au can be extracted prior to cyanidation by simpler and cheaper processes, while avoiding the difficulty of cyaniding coarse gold.

In the case of coarse-grained gold, gravity concentration is more advantageous than the amalgamation of the entire ore, since it extracts both clean and rusty gold as well as gold in sulphides.

As has been stated elsewhere, in the cyanide process the pulp may be separated into sands and slime and the two may be treated separately; or all the ore may be ground very fine and treated together by the all-slime process. The separate treatment of sands and slime, despite a somewhat lower gold extraction, is more attractive economically, especially in the case of lean ores, expensive power and

high yields of sands. The all-slime process is preferable in the case of high-grade ores with fine gold grains, cheap power and low yields of sands. Furthermore, the all-slime process can be easily mechanised and automated and requires less plant and manpower. Gold extraction is always higher with the all-slime process.

The flow-sheets combining gravity concentration, amalgamation and cyanidation are shown in Figs. 167 and 168.

Sulphide ores lend themselves advantageously to flotation which may be carried out in a variety of schemes:

(1) flotation of gold and sulphides, with tailings discarded and the concentrate cyanided;

(2) flotation to remove minerals handicapping cyanidation into the float, with the tailings cyanided;

(3) flotation of cyanided tailings in order to remove hard-to-cyanide gold (with the flotation concentrate treated pyrometallurgically);

(4) flotation after amalgamation;

(5) flotation to obtain collective, mainly gold-copper or gold-lead, concentrates to be treated pyrometallurgically.

Except for the last case, flotation will only be warranted where gold extraction is insufficient by any other processes.

A scheme using flotation is shown in Fig. 169.

The principal criterion by which to be guided in choosing a particular method for ore preparation and treatment is the proportion of gold extracted. Rough data on gold extraction by various processes are given (in per cent) below:

Pan amalgamation	65-85
Separate sand and slime treatment	89-91
Flotation and cyanidation	88-95
All-slime process	90-96

Another important factor governing the choice of a particular flow-sheet are operating costs, especially cost of power.

Approximate Energy Consumption (kWh/ton) for Medium-hard Ores

Sand percolation	0.6-0.8
Flotation (with concentrates sent to smelters)	17-25
Separate sand and slime treatment	21-29
All-slime cyanide process	28-35

With some ores the above processes either suffer incomplete gold extraction or involve increased consumption of reagents and power, and so special modifications have to be introduced into the established practices.

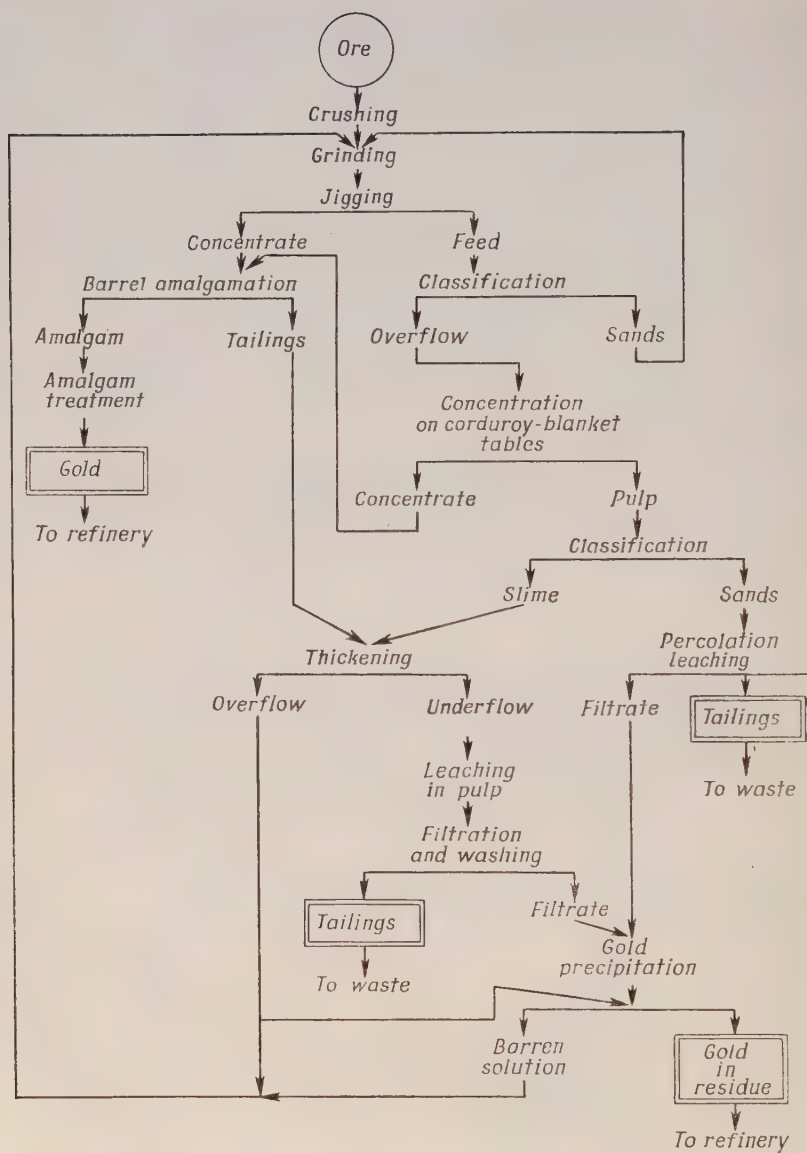


Fig. 167. Flow-sheet combining amalgamation, gravity concentration and separate treatment of sands and slime

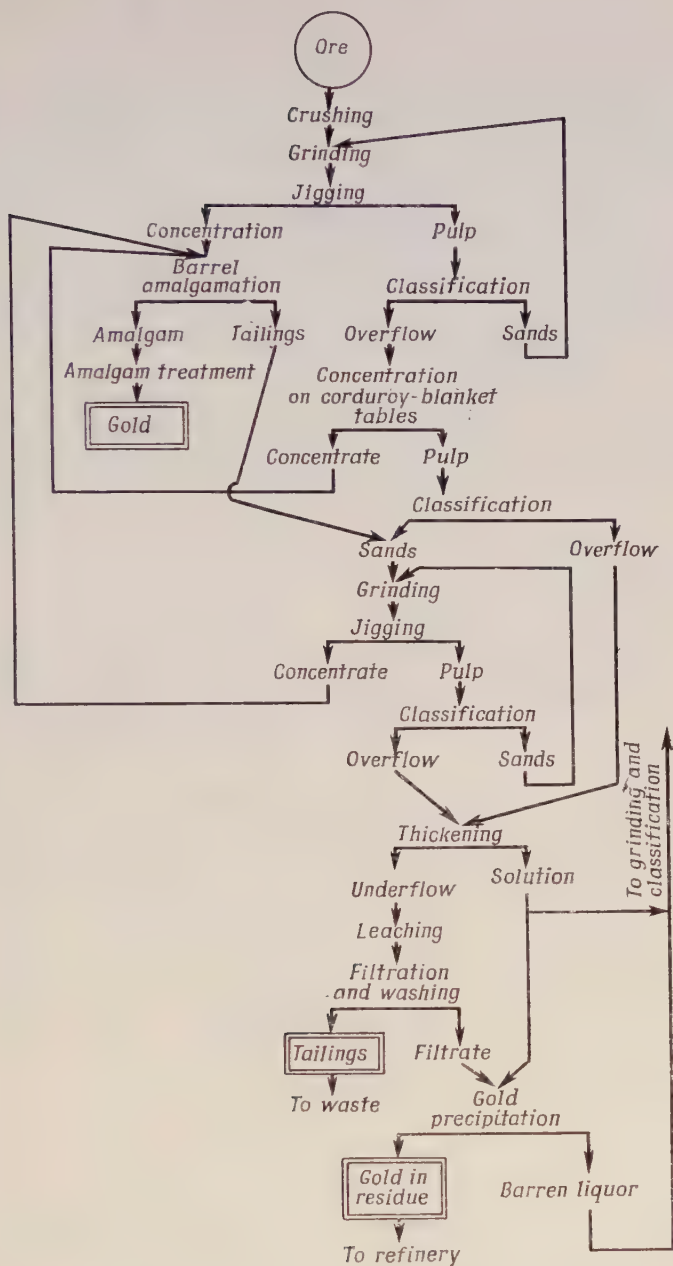


Fig. 168. Flow-sheet combining amalgamation, gravity concentration and all-slime process

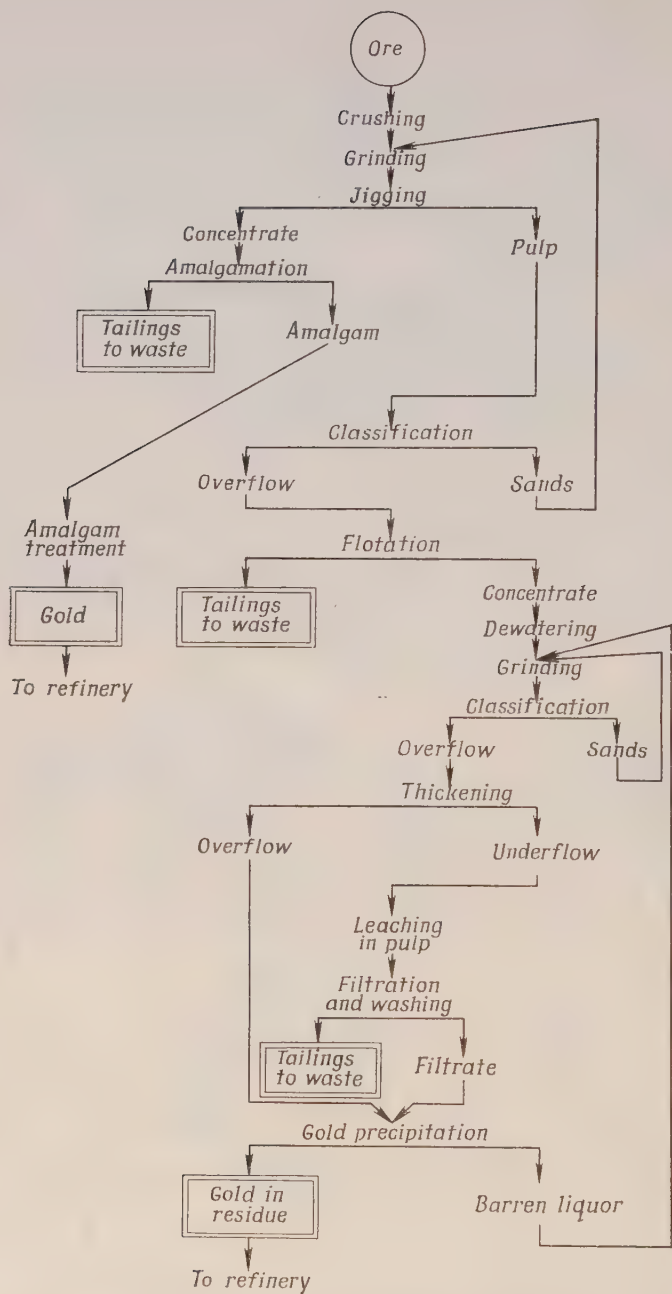


Fig. 169. Flow-sheet combining cyanidation, amalgamation and flotation

Coppery gold ores which would otherwise consume too much cyanide should be first floated to remove copper minerals, or acid-treated to leach out the copper, or given an oxidising roast to convert the copper into ferrites and then cyanided with weak cyanide solutions which attack copper mineral insignificantly.

Arsenical and antimonial ores containing red arsenic, auripigment and antimonite, are difficult to cyanide, for some of the oxygen goes to oxidise the arsenic and antimony compounds. Therefore, these ores should be either treated with weak cyanide solutions and alkalis or floated to remove the cyanides. In the latter case, some of the gold will be carried over into the flotation concentrate. The concentrate is given an oxidising roast in which a greater proportion of the arsenic is volatilised as As_2O_3 , and the calcine is cyanided. Amalgamation of these ores is handicapped by flouring. The best process for the extraction of coarse gold from arsenical and antimonial ores is gravity concentration.

Telluride ores resist both amalgamation and cyaniding. Fine grinding may be recommended for them prior to cyanide treatment. As an alternative, they may be given an oxidising roast which will decompose gold tellurides and volatilise the tellurium as TeO_2 . In cyaniding, BrCN is used together with plain cyanides (and the process is called bromocyaniding). Flotation as a preliminary treatment is also advisable, since it removes the tellurides into a relatively small quantity of concentrate which may be treated separately.

Low gold extraction is also obtained in cyaniding coaly ores such as those containing graphite. In this case, the dissolved gold is adsorbed by the coal or graphite particles and much of it is left in the tailings. In some cases, this trend may be controlled by adding some kerosene or oil to the pulp. As an alternative, the coaly fraction may be removed by flotation prior to cyanidation.

Chapter XII

AN OUTLINE OF SILVER

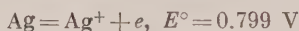
104. Properties and Uses

Silver is a white lustrous metal softer than gold but harder than copper. It has a face-centred cubic structure.

The metal melts at 960.5°C and boils at 2180°C . Silver has the highest electrical and thermal conductivities of any of the elements.

The fact that silver is in Group I of the Periodic Table and its atomic configuration identify it as a typical, predominantly monovalent metal. Di- and trivalent compounds of silver are known but are of low practical value mainly because they are strong oxidising agents and extremely unstable.

The standard electrochemical potential of silver is positive:



This is why silver will dissolve in sulphuric and hydrochloric acids only in the presence of an oxidising agent. The film of AgCl forming on the metal also adds to its resistance to hydrochloric acid. In hot nitric acid silver rapidly dissolves to form AgNO_3 with the evolution of NO and NO_2 .

Under ordinary conditions silver does not oxidise in the atmosphere. At low temperatures, the standard free energy of formation of silver oxide (Ag_2O) is negative ($\Delta G = -2.6 \text{ kcal}$). Direct oxidation, however, will not produce this oxide because of a too low rate of oxidation. Produced by any other method, the oxide decomposes on heating. Molten silver readily absorbs oxygen. On cooling and freezing, it releases a large volume of oxygen, giving rise to "sprouting" or "spitting".

In ancient times silver, like gold, served as a monetary standard. In ancient Egypt (2500 B.C.) it was considered more expensive than gold. Later, when silver came to be produced in large quantities, its price dropped. With the development of trade, silver ceased to be a monetary standard, and is now used only in subsidiary coinage.

At the present time, the chief uses of silver are based on its high electrical and thermal conductivities, high corrosion resistance, and the non-contamination of liquids with which it is in contact. It is used as a constituent of antifriction alloys employed in the aircraft industry, as a protective coating on chemical apparatus, as a backing for mirrors and light reflectors, as a source material for photographic emulsions, and also in jewelry.

105. Sources and Production of Silver

Silver occurs in nature chiefly as sulphide which may exist as the mineral argentite, Ag_2S , or as sulphosalts of the type $n\text{Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$ and $m\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ sometimes containing copper, or as oxidised ores in the form of cerargyrite, AgCl , and argentojarosite, $\text{AgFe}_3(\text{OH})_6(\text{SO}_4)_2$, and as native silver in grains differing in size.

A good proportion of silver is associated with galenite in which Ag_2S forms highly dispersed inclusions. About 75 per cent of the total silver is a by-product of lead and copper production. A relatively small quantity of silver is obtained as a by-product of gold extraction.

Silver ores proper are beneficiated by flotation and gravity concentration, and the resulting concentrates are cyanided. With properly chosen floating agents, all silver minerals except for argentojarosite are floatable. Where the content of argentojarosite is high, flotation ought not to be used.

Cyanidation can extract silver directly from native metal, cerargyrite and argentite. The other sulphides, sulphosalts and argentojarosite require a chlorinating roast with common salt to convert them into AgCl and Ag_2SO_4 prior to cyaniding.

Silver cyanidation requires solutions much higher in NaCN for the reason that ores contain much more silver than gold. Precipitation uses both zinc and aluminium dust. Some ores are treated by a combination of amalgamation and cyanidation conducted as a single operation in rod-mills.

Secondary silver is obtained from spent photographic emulsions, jewelry scrap, broken mirrors, etc.

Chapter XIII

A BRIEF OUTLINE OF THE PLATINUM GROUP

106. Properties and Uses

All metals in the platinum group have high melting and boiling points. In addition to this, rhodium, iridium and ruthenium have the highest hardness of any of the heavy non-ferrous metals (see Table 45). In fact, iridium and ruthenium are close to quenched steel in hardness. On the other hand, platinum is very ductile and resembles gold in this respect.

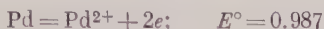
Table 45

Metal	Symbol	Colour	Crystal lattice	Density, g/cm ³	Melting point, deg. C	Boiling point, deg. C	Brinell hardness, annealed
Platinum	Pt	Greyish-white	Face-centred, cubic	21.40	1773.5	4250	47
Iridium	Ir	Silvery-white	ditto	22.42	2454	5300	172
Palladium	Pd	ditto	ditto	12.16	1553	—	49
Rhodium	Rh	ditto	ditto	12.41	1966	—	139
Ruthenium	Ru	ditto	Hexagonal, close-packed	12.20	2450	4900	220
Osmium	Os	Bluish-grey	ditto	22.48	2700	5500	—
Gold	Au	Yellow	Face-centred, cubic	19.26	1063	2950	45
Silver	Ag	White	ditto	10.49	960.5	2180	50

The platinum-group metals have about one-fifth of copper's electrical and thermal conductivities.

The platinum group of metals is in Group VIII of the Periodic Table which fact speaks of their metallic nature and a valence which may vary from 1 to 8. All the metals in the group tend to form complex anions. The various concentrated mineral acids and even aqua regia do not attack them, except for platinum and palladium, the latter being soluble also in nitric acid. The standard

electrochemical potentials are only known for three of the six metals:



When dissolved, alkalis do not attack the platinum-group metals; when molten, however, and especially, in the presence of an oxidising agent, they easily dissolve them. The platinum-group metals do not oxidise in the atmosphere, except for osmium which when powdered forms OsO_4 even at room temperature.

Here are the standard free energies of formation of some of the oxides of the noble metals (in kcal per g-mole O):

Au_2O_3	Ag_2O	PtO	PdO	OsO_4
13.0	-2.6	-13.0	-14.4	-17.6

When compacted and especially finely divided, the platinum-group metals are capable of absorbing gases. Palladium can absorb more than 700 times its own volume of hydrogen at room temperature, and platinum about 70 times its own volume of oxygen at 450°C . This property accounts for an increase in the catalytic activity of the platinum-group metals in some chemical reactions with reduction in their size or, which is the same, with an increase in their surface area.

Platinum was discovered in the 18th century. The other platinum metals, except for ruthenium, were discovered in 1803-1804, while ruthenium was first isolated by Claus of Russia in 1844.

In the 19th century the platinum metals were mainly used in jewelry. Today they have found many industrial uses. Platinum wire, for example, goes to make electric-furnace resistors, thermocouples and resistance thermometers. An alloy of platinum and 10 per cent rhodium is used to make thermocouples.

Palladium and its platinum alloys are used in jewelry, electrical engineering and medical instrumentation. Rhodium and palladium are also used as coatings for light reflectors operating at elevated temperatures. Although they reflect less light than does silver, they have the advantage of resisting to tarnish in the presence of hydrogen sulphide.

Alloys of platinum and iridium are extremely hard and wear-resistant. Incidentally, the international prototype metre kept in Paris is made from an alloy of 90 per cent platinum and 10 per cent iridium. Still harder alloys of osmium and iridium go to make parts of precision mechanisms, such as chronometer shafts.

Finely divided platinum metals are used as catalysts in some of the chemical processes, for example in the production of nitric acid from ammonia.

107. Sources of the Platinum Metals

Platinum chiefly appears in metallic grains more or less alloyed with other metals. Sometimes it is found as odd-shaped large nuggets or cubic crystals.

The composition of native platinum differs widely. Sometimes it is ferro-platinum (80-82 per cent Pt and 12-13 per cent Fe). In other cases it is known as polyxen which carries much less iron. Cuproplatinum, nickel and palladium platinum are of more seldom occurrence. Their names imply their composition, although in all cases they contain some iron. Apart from natural alloys, there are platinum minerals, such as sperrylite, PtAs_2 ; cooperite, PtS ; and braggite, $(\text{Pt}, \text{Pd}, \text{Ni})\text{S}$. Similar to native platinum are nevyanskite which is an alloy of 47-77 per cent Ir, 20-45 per cent Os and also Ru, Rh, and Pd (known as osmiridium) and sysertskite (known as iridosmine).

Aside from braggite, palladium occurs in stibiopalladinite (Pd_3Sb) or as solid solution in sulphides of nickel and iron.

Minerals of the platinum metals are often associated with pyrrhotite, pentlandite and chalcopyrite; their deposits are found in basic and ultra-basic rocks—gabbro and norite.

Like gold, platinum occurs in placers which in Russia had been the source of over 90 per cent of the platinum mined until 1915. Today a good proportion of the annual production comes as a by-product in the electrolytic recovery of nickel and copper.

The principal processes for the recovery of the platinum metals are gravity concentration, flotation and amalgamation. Gravity and flotation concentrates often carry all the platinum metals and also gold and silver, and they are treated at gold refineries. Pure mercury attacks platinum slowly and incompletely, and so a modification of amalgamation is applied in which instead of pure mercury, use is made of zinc amalgam, and the pulp is acid-treated. The acid scours platinum grains of the surface oxides of base metals. The hydrogen evolved by zinc in an acid medium cleans the platinum of the chemisorbed oxygen which prevents amalgamation. Being reduced by zinc on the surface of platinum grains, copper promotes their wetting by mercury.

Chapter XIV

REFINING OF GOLD AND SILVER BULLION

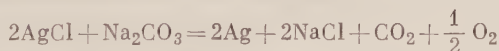
108. General

All classes of bullion that come for refining, including bars, rich gravity concentrate, cyanide precipitate, slimes from the electrolytic recovery of copper and nickel, amalgamated metal and also industrial and domestic scrap, contain both gold and silver intimately associated. Therefore, refining processes must provide not only for the elimination of the base metals present in the alloy, but also for the "parting" or separation of the gold and silver. Furthermore, the bullion must be blended or mixed in definite proportions so as to obtain a melt of prescribed purity or fineness*.

The blending of the source bullion is performed in tilting crucible furnaces which may be oil, gas or electric heated, and also in graphite-grog and carbon crucibles resistant to the fluxes usually used. Gold-silver alloys containing less than 300 parts gold and more than 700 parts gold are treated separately.

The separation of the gold and silver in bullion can be effected either by dry, wet, or electrolytic methods.

The dry method was at one time embodied in the chlorination (Miller) process applicable to bullion containing 600 to 700 parts gold. In this process chlorine gas is passed through the molten metal, converting the silver and base metals into chlorides. The silver chloride which has a melting point of 455°C floats on the surface of the molten gold and is baled off at intervals. The chlorides of the base metals either pass off as fumes or dissolve in the silver chloride. As a result, gold 996 or 997 fine can be obtained. The silver chloride is remelted with sodium carbonate to reduce it to metallic silver according to the reaction



The slag and other by-products of the process have to be re-treated for the recovery of their silver content by complicated hydrometallurgical methods. Today, the Miller process is solely employed to remove some base metals. The reasons for its falling into disfavour

*The purity or fineness of a bullion in the Soviet Union and several other countries is expressed in parts per thousand while in many other countries in carats (twenty-fourths). The impurities are usually referred to as "base metals" or simply "base".

are considerable losses of the values and low fineness of the gold obtained.

The wet method is based on the solubility of silver and the insolubility of gold in sulphuric acid. This method successfully parts bullion containing 2 to 4 parts of silver to 1 part of gold. Bullion higher in gold has to be "diluted" with silver. The bullion in granulated form is treated with boiling concentrated sulphuric acid. The silver and base metals pass into solution, and the gold settles as a brown-black residue. The clear solution of silver is ladled or siphoned, and the gold residue is repeatedly boiled with fresh concentrated acid to remove the remaining silver and base metals. The gold is then pressed, dried, melted and cast into bars having a fineness of 996 to 998 and containing the bulk of the platinum metals. The silver from the solution may be recovered by precipitation with copper. The sulphuric-acid process suffers from a number of drawbacks among which are much time required to dissolve the silver, high requirements in acid, and insufficient separation of the metals. Today, this process is only employed to remove the bulk of the base metals prior to electrolysis.

The electrolytic method is most perfect of the three. In the case of bullion in which silver predominates it involves two stages of electrolysis: during the first stage, the bullion is dissolved at the anode with metallic silver depositing on the cathode and the gold passing into slime; during the second stage, the slime is remelted and dissolved at the anode in another cell, with the gold depositing on the cathodes. It is usual to refer to the two processes as "silver refining" and "gold refining", the latter being also employed directly for the treatment of bullion in which gold is the predominant metal.

109. Silver Refining by Electrolysis

The bullion treated by this system, known as the Moebius process, ranges from a few points of gold, doré silver, up to 350 parts per 1000. Before electrolysis, the molten metal is blown with air or chlorine gas in order to remove the bulk of the base metals. The electrolyte is a 1- to 3-per cent solution of silver nitrate containing 0.5 to 1 per cent free nitric acid.

The bullion is cast into rectangular plates which serve as the anodes. The cathodes are thin, rolled strips of pure silver or aluminium. The anodes and cathodes are placed in tanks of hard fibre, porcelain or earthenware. Hard-fibre tanks are usually placed in wooden containers as a protection against mechanical injury. The anodes are suspended in muslin bags which serve to collect the undissolved metal and prevent contamination of the deposited silver.

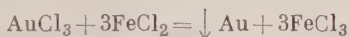
Under current action, the silver, copper, lead, bismuth and other metals are dissolved at the anode. The gold remains in the muslin bags in a brittle brownish-black mud, or black gold, which also contains platinum metals, some silver, tellurium, sulphur and other insoluble impurities.

The silver is deposited on the cathodes in a loose coarse crystalline form easily removed from the cathodes to fall to the bottom of the refining tank.

Anodes up to 12 mm thick will be treated for about twenty-four hours, after which the undissolved metal is returned for remelting, the anode mud is removed from the bags, and the silver crystals are scooped from the tank bottom with aluminium skimmers.

The electrolyte is replenished at regular intervals so as to prevent its contamination with impurities, mainly copper whose content in the electrolyte should not exceed 4 or 5 per cent. The spent electrolyte is treated for the recovery of silver, platinum and platinum metals. The silver residue is washed, briquetted and remelted, giving a product 999 fine or even better.

The black gold is removed from the bags and treated with nitric acid to dissolve the remaining silver, selenium and tellurium before it is remelted into anodes for gold refining; the platinum metals are left in the black gold. If their content is high, it will be profitable to dissolve the anode black gold completely in aqua regia and to precipitate the gold with iron chloride:



The gold residue should then be filtered, and the platinum from the filtrate precipitated with iron. A further treatment should also be given to the clear solution so as to recover the platinum metals contained in it.

110. Gold Refining by Electrolysis

This system, known as the Wohlwill process of gold refining, is applicable to bullion containing 800 or better of gold per 1000.

The electrolyte is a 7- to 10-per cent solution of gold chloride containing some free hydrochloric acid. The AuCl_3 is prepared in separate diaphragm-type tanks by dissolving gold at the anode in hydrochloric acid. Sometimes the electrolyte is produced chemically, by dissolving gold in aqua regia and digesting the solution to drive off the nitric acid.

The anodes are rectangular plates, and the cathodes are of corrugated gold foil. The cells are of porcelain or fire-resistant glass. They are placed under an exhaust hood on a range which heats the electrolyte to 55 or 65°C.

The gold dissolves at the anode and is deposited on the starting sheets as a dense and hard layer. Some gold also precipitates at the bottom of the cell due to the simultaneous formation of uni- and tri-valent ions of gold at the anode:



The silver is changed to insoluble chloride which forms a strong coating on the anodes, thus rendering them practically insoluble. To loosen the chloride coating, a non-symmetrical alternating current is used, obtained by connecting a direct-current generator in series with an alternating-current source. The non-symmetrical alternating or pulsating current makes possible the refining of gold bullion 800 fine. A similar passivating action on the anodes may be produced by an excess of lead, selenium and tellurium in them.

The electrolyte is changed at regular intervals to prevent the excessive accumulation of impurities, especially copper.

The foul electrolyte contains gold and also the platinum metals which dissolve at the anode together with the gold without depositing on the cathode, and the base metals. In treating the foul electrolyte, first the platinum is completely precipitated from it with a saturated solution of ammonium chloride:



The washed precipitate of platinum-ammonium chloride is calcined to produce platinum sponge. The complete recovery of platinum requires a separate operation. After the precipitation of platinum, the gold is precipitated with copper, and the cement gold is returned for gold refining.

111. Refining of the Platinum Metals

Platiniferous materials come for refining as gravity concentrates of placer platinum, slimes from the electrolytic refining of nickel, by-products of gold refining, amalgamated metal, scrap, etc.

From gravity concentrates and similar platiniferous materials the bulk of the platinum is recovered by treating them with aqua regia first while cold and then with concurrent heating. Passing into solution are the bulk of the platinum, some iridium as chloro-metallic acids of the type H_2MCl_6 and some palladium as H_2PdCl_4 . Little rhodium and ruthenium is dissolved to form compounds of the type H_3MCl_6 .

The insoluble residue contains all the osmium, the bulk of the iridium, rhodium and ruthenium, and the remaining platinum.

If the source material has not been sufficiently ground, mineral particles—osmiridium and large platinum grains—will remain in it. The residue is dispersed and re-treated with aqua regia.

The solution is digested with sulphuric acid, or treated with oxalic acid, a sugar solution and other reducing agents in order to reduce the iridium compounds to metallic iridium.

During the next step, the platinum is precipitated with ammonium chloride according to the reaction given earlier. The platinum-ammonium chloride, also carrying some iridium, is washed, dried and calcined with the temperature gradually raised to 1100-1200°C. The product of this calcination is platinum sponge:



When the solution from the precipitation of the platinum with ammonium chloride is left standing, the iridium and the remaining platinum come at last down as $(\text{NH}_4)_2\text{IrCl}_6$. This is filtered, washed, dried and calcined, giving iridium moss.

The platinum sponge and iridium moss are then redissolved in aqua regia and the solution is precipitated to form ammonium salts of the respective chlorometallic acids. After the precipitation of the platinum and iridium, sulphuric acid is added to the solution to precipitate the palladium, rhodium and ruthenium with iron or zinc.

From H_2PdCl_4 the palladium is precipitated with ammonia and then with hydrochloric acid.

Rhodium may be recovered by the Lebedinsky process. To this end, the solution is neutralised with an alkali and sodium carbonate and is then treated with sodium nitrite:



The rhodium passes into solution; the solution is filtered to separate the hydrates and basic salts of the heavy metals. Some acetic acid is then added to the filtrate, and the latter is treated with ammonium chloride. This throws the rhodium down as a crystalline residue:



The ammonium salt of rhodium hexanitrite is treated with an aqueous solution of sodium hydrate, and some ammonia and ammonium chloride is added to throw down rhodium triaminnitrate as a crystalline residue which is then changed to triaminchloride by heating in hydrochloric acid. The triaminchloride is calcined in a hydrogen atmosphere at 900°C until it forms rhodium moss.

Osmium is recovered from the insoluble residues of the original platinum treatment by aqua regia. The residues are sintered with BaO_2 , the sinter powdered, and the powder treated with a mixture of hydrochloric and nitric acids in a distilling flask. The osmium tetroxide passes off as fumes which are caught by a solution of sodium hydrate as Na_2OsO_4 . The solution is then treated with hyposulphite to reduce it to six-valent osmium and then with ammonium chloride. The osmium is thrown down as $\text{OsO}_2(\text{NH}_3)_4\text{Cl}_2$, and the latter is washed, dried and calcined in a hydrogen atmosphere, giving osmium moss.

Part Five

THE METALLURGY OF THE LIGHT-WEIGHT METALS

Chapter XV

THE METALLURGY OF ALUMINIUM

112. General

Aluminium is the principal member of the group of light-weight metals. It is a silvery-white metal, and its atomic configuration is 2-8-3. The presence of three electrons on the outer shell accounts for the fact that aluminium is trivalent in basic compounds and univalent in some others.

The most important property of aluminium is its low specific gravity which is 2.7 or one-third of iron's. Its other properties of importance to electrical engineering and the motor industry are high electrical and thermal conductivities (see Fig. 1). Furthermore, it is plastic, chemically resistant to the action of nitric and organic acids, though it succumbs to alkalis. When aluminium surfaces are exposed to the atmosphere, a thin invisible oxide skin forms immediately which protects the metal from further oxidation. This self-protection gives aluminium its high resistance to corrosion.

Although aluminium has a melting point of 660°C, it takes much heat to melt it owing to its high latent heat of fusion and heat capacity.

Aluminium is an easily deformable metal because it has a face-centred cubic lattice. Annealed aluminium is of low strength, but it can be strain-hardened by cold rolling.

The properties of aluminium vary with its purity. Its corrosion resistance and electrical conductivity are at their highest when the metal contains little, or no, impurities and additions. On the other hand, additions of other metals may considerably improve its other properties, especially strength and castability. Such additions are magnesium, silicon, copper, zinc and manganese. The mechanical properties of wrought aluminium alloys may be improved by adding magnesium, copper and manganese. This, incidentally, applies to duralumin which after ageing has the same strength as structural carbon steels.

Cast aluminium alloys usually contain considerable amounts of silicon which improves their fluidity when molten and reduces volumetric shrinkage. The mechanical properties of cast aluminium alloys are, however, inferior to those of wrought aluminium alloys. Data on the mechanical strength of aluminium, its alloys and two grades of steel are given for comparison in Table 46.

Weight for weight, aluminium alloys are stronger than mild steels and approach alloy steel.

Table 46

Mechanical Properties of Aluminium and Other Metals

Metal	Main constituents, per cent						Other elements, per cent	Temper	UTS, kg/sq mm	Elong., per cent	HB	UTS/sp. gr.
	Cu	Mg	Mn	Al	Fe	C						
Aluminium	—	—	—	99.99	—	—	—	Annealed	5	50	15	1.9
Alloy Д16	4.5	1.5	0.6	Re-maind-er	—	—	—	Age-hardened	50	20	110	18.5
Alloy B95	1.7	2.3	0.4	ditto	—	—	Zn, 6	Hardened and annealed	60	12	150	21.2
Steel Ct. 3	—	—	0.3	—	99.5	0.2	—	Normalised	45	22	150	5.7
Alloy steel	—	—	0.3	—	94.4	0.3	Ni, 3.5	Quenched	150	6	300 and more	19.3
							Cr, 1.5	Annealed	100	15		12.8

Aluminium alloys stand up well to impact loads as they absorb three times as much energy as does steel.

All these properties have since long won aluminium an outstanding place in the aircraft industry. During the last few decades aluminium alloys have gained ever more ground in the motor industry and also in the manufacture of railway rolling stock. Passenger carriages built of aluminium are light in weight, and so trains have a shorter braking distance which fact adds materially to the safety of traffic.

In shipbuilding, aluminium alloys are made into superstructures, funnels, masts, boats, etc., thereby increasing the cargo-carrying capacity and reducing the draught of vessels, which is of special importance to river craft. At the same time, vessels gain in stability owing to the fact that the centre of gravity is now placed lower.

Aluminium alloys have become the principal materials in the manufacture of internal-combustion engines owing to both light weight and high thermal conductivity.

In electrical engineering, use is made of both pure aluminium and some of its current-conducting alloys. Although aluminium is appreciably inferior to copper in electrical conductivity, some applications give preference to aluminium conductors which, having equal resistance, are lighter than copper ones. This feature is of vital importance in the case of overhead power transmission lines, since this makes it possible to reduce the number of supports required. Electrical uses also include aluminium rectifiers, capacitors and other components.

Modern instruments are inconceivable without aluminium, and so are cine and photographic equipment, radio components, etc.

Owing to its high affinity for oxygen, aluminium can reduce most oxides to the respective metals. This property has become the basis of the aluminothermic process—the production of various rare metals from their oxides by reducing them with powdered aluminium. This process is, for example, used to produce pure chromium, vanadium, strontium, barium, and lithium.

Low-grade aluminium goes to deoxidise some steels. Aluminium is fabricated into storage vessels for acetic, oleic, stearic and other organic acids, apparatus for the production of boric acid, fats, alcohols, oils, varnishes, rayon, esters, glycerine, celluloid, etc. Aluminium equipment is also used widely at dairies, breweries, sugar refineries and pastry cooking owing to the fact that aluminium is free from harmful physiological action. Aluminium foil goes to pack various food products.

Since 1945, aluminium and its alloys have come to be used in buildings, furniture and household goods. In buildings, aluminium is made into roofing, window frames and railings.

Powdered aluminium is used as a paint, while jewellers anodise aluminium alloys to give them the colour of gold, silver or other hues. Anodised aluminium is manufactured into watch cases and decorations.

Aluminium of very high purity and some of its alloys are often used as coatings for light reflectors and as a backing for mirrors, because when suitably treated chemically and electrolytically the metal acquires a very high reflectance.

Last but not least, the capsules and various parts of artificial Earth satellites and space probes are made from aluminium alloys. All of the above uses have considerably spurred the production of aluminium.

Aluminium compounds are used in various fields of technology. One such compound, fused aluminium oxide or corundum (Al_2O_3), is an excellent abrasive material and is fabricated into grinding stones and wheels. Pure aluminium oxide serves as a source material for refractories, artificial ruby, and high-quality dental cements. Anhydrous aluminium chloride is used as a catalyst in oil refining and in the synthesis of some organic materials. Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$, serves as a coagulating agent in water purification. Wide use is made in the textile, tanning and paper industries of alums (such as $\text{K} \cdot \text{Al}[\text{SO}_4]_2 \cdot 12\text{H}_2\text{O}$).

113. Sources of Aluminium

Although aluminium is the world's most abundant metallic element, it does not occur native owing to its high affinity for oxygen. According to Fersman (U.S.S.R.), there are about 250 aluminium-bearing minerals, mainly silicates and oxides. At present, the term "ore" as far as aluminium is concerned is applicable to bauxite, nepheline, alunite, kaolin, and cyanite.

Bauxite is the base ore for aluminium reduction. Bauxite is an earthy mineral and never crystallised. It is essentially a mixture of aluminium hydroxide, iron oxide, hydroxide and silicates, quartz, kaolinite, titanium compounds, carbonates of calcium, iron and magnesium, and also small amounts of sodium, potassium, zirconium, chromium, phosphorus, vanadium, gallium and other compounds, in subordinate amount.

The chemical composition of bauxite varies within broad limits. The grade of a bauxite ore depends on its alumina and silica contents and also on the mineralogical form of its aluminium hydroxide, the quality being higher with increasing Al_2O_3 content and decreasing SiO_2 content.

Bauxite ores likewise vary widely in physical properties even in the same grade of ore. The colour of bauxites varies considerably

depending on the iron-oxide content. They may be roughly classed on the basis of their impurities as follows: (1) high in iron and low in silica (red varieties); (2) low in iron and high in silica (white and gray bauxites); and (3) iron and silica contents about the same. The most commonly found bauxites are in the brown and brick-red variety. Their specific gravity ranges from 1.2 for porous and loose low-iron low-silica bauxites to 3.5 for high-iron and stony bauxites. The hardness of bauxites may be anywhere from 2 to 7 Brinell. This

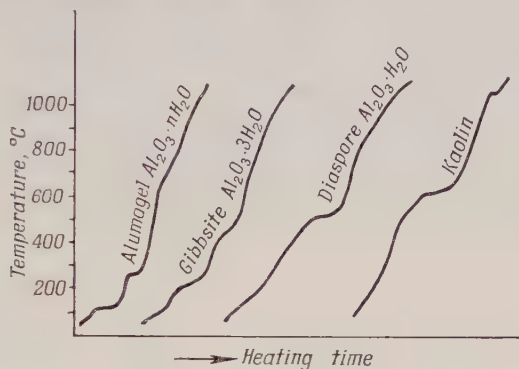


Fig. 170. Heating curves for clay and aluminium hydroxide

diversity in appearance and physical properties handicaps prospecting for bauxites. A feature that sets them apart from clays is that they do not mix with water.

Mineralogically, bauxites differ from clays in that in the latter aluminium is present as kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and as other aluminosilicates. In bauxites, on the other hand, hydrated oxide of aluminium is to be found. The latter may be present in three mineralogical varieties: as boehmite and diaspore, both answering the chemical formula $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and as gibbsite which has the formula $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The mineralogical form in which aluminium may be present has a direct bearing on the way a given ore will be processed. Therefore, bauxite ores are commercially classed into boehmitic, diasporic, gibbsitic and mixed.

A convenient method for the mineralogical identification of bauxites has been developed by Kurnakov and Urazov of the U.S.S.R. Its basis is the difference in dehydration points: gibbsite begins to lose its water at 202-205°C, diaspore at 509-555°C, and kaolinite at 558-605°C. Dehydration uses some heat, which fact is shown as a flat on a heating curve (see Fig. 170).

Nepheline may be described by the chemical formula $(\text{Na}, \text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and is found in urtites and apatites. Flotation

of apatite leaves nepheline in the tailings. When nepheline is converted into alumina, sodium carbonate and potash are obtained as by-products. The approximate chemical composition of nepheline concentrates is as follows: Al_2O_3 , 30 per cent; SiO_2 , 43 per cent; $\text{Na}_2\text{O} + \text{K}_2\text{O}$, 20 per cent; and CaO and Fe_2O_3 , 3 per cent each. Although nepheline is low in Al_2O_3 , it may well be used as a source of both alumina and potash, with the wastes utilised in cement production.

Alunite is a hydrous sulphate of aluminium and potassium, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$, which may also include sodium. Its composition is as follows: Al_2O_3 , about 20 or 21 per cent; SiO_2 , 41-42 per cent; F_2O_3 , 4 or 5 per cent; $\text{Na}_2\text{O} + \text{K}_2\text{O}$, 4.5 or 5 per cent; SO_3 , 22 or 23 per cent; and H_2O , 6 or 7 per cent. It may also be used as a source of both alumina, sulphates, and potash.

Kaolin and clays are of the composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and also contain some impurities, such as silica, and oxides of calcium, magnesium and iron. In fact, common clays are very impure kaolins. High-grade kaolin is a source material for the manufacture of silicon-aluminium alloys. It contains 36 to 39 per cent Al_2O_3 .

Cyanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is not used for alumina production, but it is a valuable source material for the direct smelting of silicon-aluminium alloys (see below).

114. Historical Survey

Aluminium was first isolated by Oersted of Denmark in 1825. It was up to 1845, however, that Wöhler of Germany had been able to produce aluminium in amounts sufficient to determine most of its properties. Its properties proved so attractive that scientists in several countries made attempts to develop commercial processes for the manufacture of aluminium. In 1854 Deville of France came out with the first commercial process for the production of aluminium by the reduction of aluminium bichloride with sodium with concurrent heating. In Russia work on processes for the manufacture of aluminium was conducted by Beketov, an outstanding physical chemist. In his doctorate thesis published in 1865 he experimentally proved the feasibility of a process in which aluminium could be produced by the reduction of cryolite, Na_3AlF_6 , with magnesium. This process was in use commercially at the aluminium works in Gmelingen (Germany) in the 1880s.

In 1886 Héroult in France and Hall in the United States independently patented a process which ousted all other processes from the field. Based on the electrolytic decomposition of alumina dissolved in a liquid bath of cryolite, it has become a regular industrial practice since 1888.

The advent of the electrometallurgical method spurred the search for various methods for the preparation of pure aluminium oxide which had heretofore been used solely in the textile industry and in grinding.

Today there exist at least several hundred patents for the preparation of aluminium oxide, but commercial use is made of very few. The oldest one is the method suggested by Le Chatelier in 1858-60. By this method, bauxite and sodium carbonate are roasted at elevated temperature, thus obtaining solid sodium aluminate. The original process has more than once been modified by a number of investigators, including Morin, Mueller, Peniakoff, Packard, Yakovkin, etc.

Another widely practised method of alumina preparation which has largely supplanted the Le Chatelier process is the Bayer process developed by K. I. Bayer, a Russian chemist, and first applied industrially at a textile chemical works in St. Petersburg in 1899. Since then the Bayer process has been perfected by investigators in Germany, the United States and the Soviet Union.

For the electrolytic process as it stands today, a primary requisite is a source of cheap electric power, since enormous blocks of power are required. Furthermore, the process uses great quantities of high-purity alumina and cryolite and also ashless carbon electrodes. The three source materials have to be prepared by fairly complicated methods. Therefore, the production of metallic aluminium on a commercial scale has four essential steps: (1) the preparation of high-purity alumina; (2) the preparation of cryolite; (3) the manufacture of electrodes; and (4) the manufacture of metallic aluminium from alumina.

Chapter XVI

THE PREPARATION OF ALUMINA, CRYOLITE AND CARBON ELECTRODES

115. Properties of Alumina and a General Outline of Its Preparation

In the Soviet Union alumina is available in four grades, designated Γ_{00} , Γ_0 , Γ_1 and Γ_2 , respectively. The first three are used in the production of aluminium. The content of impurities in them is limited as follows: silicon, up to 0.16 per cent; iron oxide, maximum 0.04 per cent; Na_2O , maximum 0.6 per cent; calcium oxide, maximum 0.04 per cent; loss on ignition, maximum 1 per cent.

Stringent requirements such as these have been necessitated by the fact that the silicon, iron and other impurities of alumina are more electropositive than aluminium and would deposit on the cathode during electrolysis, thereby contaminating the metal. Oxides of electronegative metals (K_2O , Na_2O , etc.) involve additional consumption of expensive fluorides. Water likewise has a detrimental effect on the electrolytic process: contact between hydrated oxides of aluminium with the liquid bath would cause spitting and the decomposition of the fluorides. Accordingly, the alumina used in the production of aluminium ought not to contain excess moisture or absorb it in prolonged storage.

Anhydrous oxide of aluminium is a chemically stable compound melting at 2050°C and boiling at 2980°C . Of the many modifications, only two are important industrially.

The first, known as alpha-alumina or corundum, occurs as opaque or colourless crystals. Transparent species of corundum, tinted with small amounts of other oxides, are regarded as gems (ruby and sapphire). All hydrated oxides of aluminium, when heated to over 1200°C are changed to alpha- Al_2O_3 which will not absorb moisture even in prolonged storage. Corundum is very hard and ranks ninth in hardness, next to diamond.

Another modification, gamma- Al_2O_3 , does not occur in nature. It is formed when gibbsite (or boehmite) is dehydrated in the temperature range $500\text{--}900^\circ\text{C}$. When heated to above 900°C , gamma- Al_2O_3 slowly changes to alpha- Al_2O_3 . As distinct from the first modification, gamma-alumina is highly hygroscopic.

Alumina is an amphoteric oxide. Hydrated oxide of aluminium occurs in two forms. One of them is usually ascribed the chemical formula $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; sometimes it is regarded as a hydroxide corresponding to the formula $\text{Al}(\text{OH})_3$. The same hydroxide may be presented as tribasic orthoaluminic acid, H_3AlO_3 . The other

form is usually presented as $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, although it is sometimes regarded either as an alkali (AlOOH) or as metaaluminic acid, HAlO_2 .

Hydroxide of aluminium reacts with acid solutions as a base and forms salts:



With alkaline solutions hydrated oxide of aluminium reacts as acid and forms alkali salts of aluminic acids known as aluminates:



At elevated temperatures aluminium oxide reacts with various alkali and alkali-earth compounds to form respective aluminates (sodium metaaluminate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$; calcium metaaluminate, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, etc.). These properties of aluminium oxide are utilised in the various processes for alumina preparation.

The most commonly used processes for alumina preparation may be classed into (1) electrothermic; (2) acid, and (3) alkaline.

In *electrothermic processes*, alumina is prepared by smelting a mixture of ore and a reducing agent in electric furnaces so as to reduce the impurities and to obtain molten alumina. These processes have not found any appreciable use in the aluminium industry, for they require large amounts of electricity and may only be employed where power is cheap. Furthermore, the alumina prepared by thermal methods fails to meet the requirements of the electrolytic production of aluminium.

In *acid processes* the ore is treated with a solution of a mineral acid (H_2SO_4 , HCl , etc.). The treatment produces soluble salts, such as $\text{Al}_2(\text{SO}_4)_3$, AlCl_3 , etc., and the bulk of the impurities remains undissolved. After separation, the aluminium salt solution is decomposed to throw down hydrated oxide of aluminium. The latter is calcined to give alumina.

In acid processes of alumina preparation the silica appears in the residue, and so the alumina is separated from it with relative ease and completely. On the other hand, some of the iron oxide and titania pass into solution together with the aluminium oxide. Salts of iron, titanium and aluminium are very close in properties, and their separation is a difficult operation.

Acid processes are used commercially on a limited scale because they require expensive acid-proof apparatus and the regeneration of acid for re-use is complicated and incomplete.

Alkaline processes depend for their effect on the treatment of bauxites with NaOH or Na_2CO_3 with an addition, in some cases, of lime or limestone. The treatment produces sodium aluminate

soluble in water. The sodium aluminate is separated from the residue. In the case of nephelines, soluble aluminate can be obtained by treating the ore with limestone alone. Next, the sodium aluminate is decomposed to obtain aluminium hydroxide. The latter is calcined to alumina, and the remaining liquor is returned to the process.

In alkaline processes, the oxides of iron, titanium and calcium contained in the ore are practically unattacked and are left as a residue which can be easily separated from the sodium aluminate. The silica present in the ore reacts with alkalis for which reason some of the alkali and alumina may be lost and the resulting alumina may be contaminated. This is the reason why alkaline methods are most often applied to ores containing small quantities of easily soluble forms of silica. The ferric oxide and titania present in the bauxite have but an insignificant effect on the process, affecting solely its economics (consumption of power, steam and handling facilities).

116. The Bayer Process of Alumina Preparation

While working in Russia in the latter half of the 19th century, Bayer established that the addition of aluminium hydroxide to aluminate solutions would decompose the latter and that the remaining liquor after evaporation would dissolve the alumina present in the ore, if this was done in steam-heated autoclaves at a temperature of 160 to 170°C. This invention made to meet the needs of the textile industry was later utilised in the aluminium industry of Russia, Western Europe and America.

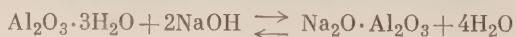
The theory of the process has been derived by the All-Union Aluminium and Magnesium Institute and the Ural Chemical Research Institute which have also extended the process to cover specifically Soviet bauxites. A flow-sheet for the Bayer process is shown in Fig. 171.

In practice, run-of-mine bauxite is crushed and then wet-ground in ball mills. The charge to the ball mill contains bauxite, aqueous sodium hydroxide and recycled or return liquor. Sometimes, a little lime is added to the charge to facilitate grinding.

The mixture of ground bauxite and recycled liquor (raw pulp) is digested. The purpose of digestion is to dissolve the aluminium oxide present in the bauxite without dissolving the other constituents (silica, titania, etc.).

Digestion involves the following principal reactions.

When mixed with sodium hydroxide at over 100°C, aluminium hydroxide forms a solution of sodium aluminate:



The ferric oxide of the bauxite is unaffected by the sodium hydroxide and is left as a residue, called red mud. Part of the silica is

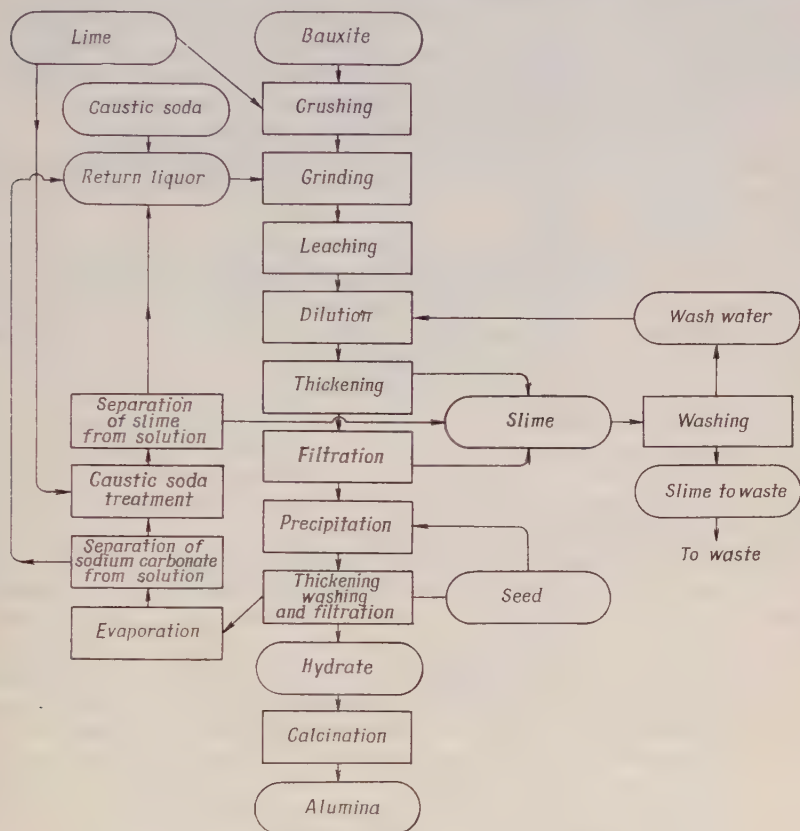
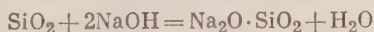
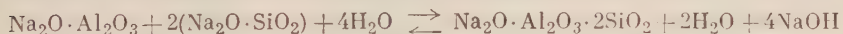


Fig. 171. Simplified flow-sheet of the Bayer process

dissolved and reacts with the sodium hydroxide to form sodium silicate:



The sodium silicate reacts with the sodium aluminate solution to form insoluble double aluminium-sodium silicate:



As a result, no impurity from silica is left in the sodium-aluminate liquor, but some sodium hydroxide and dissolved aluminium

oxide is lost. For this reason, the digesting treatment should preferably be applied to bauxites relatively low in silica.

The titania of the bauxite, of which as little as 1 or 2 per cent is present, is unaffected by the digesting treatment, while the impurities V_2O_5 , Cr_2O_3 and Ga_2O_3 pass into solution. Gallium trioxide may be partly precipitated from solution later in the process. The remaining compounds are accumulated in the liquor and may come down together with alumina, thus contaminating it.

Some bauxites contain sulphur compounds which react with sodium hydroxide, thereby handicapping the subsequent stages of the process.

The digesting treatment is carried out in autoclaves—strong steel vessels capable of withstanding high pressures at a temperature of up to 250°C and fitted with some means for stirring the pulp. The autoclaves most commonly used commercially are of the steam-bubbling type (Fig. 172) very simple in construction. Live steam is admitted through a nozzle 1. Rising to the surface, steam bubbles heat and stir the pulp. The contents of the autoclave are squeezed through a vertical pipe 2. Industrial autoclaves, also known as digesters, are available in capacities from 25 to 35 cubic metres, with a diameter of 1.6 to 2.3 metres, a height of 13.5 metres and a total weight of 17 tons.

Some alumina producers employ autoclaves fitted with mechanical stirrers and heated with steam passing through coils or jackets. These autoclaves suffer from a number of drawbacks: there is some difficulty in providing reliable shaft seals preventing leakage of liquor and loss of pressure along the shaft where the latter passes through the casing; the pulp is heated more slowly and a heat-absorbing scale forms on the walls; shut-downs for repairs are long and frequent and the equipment is less reliable in service.

Live-steam autoclaves are free from these drawbacks, but the pulp in them is diluted with steam which fact impairs the efficiency of the treatment.

The digesting treatment may be carried out intermittently in a single autoclave and will then include the following operations: charging of the pulp; heating of the pulp to the requisite temperature; digestion proper; and discharging of the autoclave.

Soviet alumina plants mainly operate on a continuous basis, using batteries of autoclaves connected in series. Apart from qualitative advantages, the continuous digestion lends itself readily to automation. A flow-sheet for continuous digestion is shown in Fig. 173.

From a mixer 1 the feed is transferred by a pump 8 into tubular heaters 2 where the material is heated by steam from the separators. The heated pulp is allowed to pass through a series of autoclaves 3.

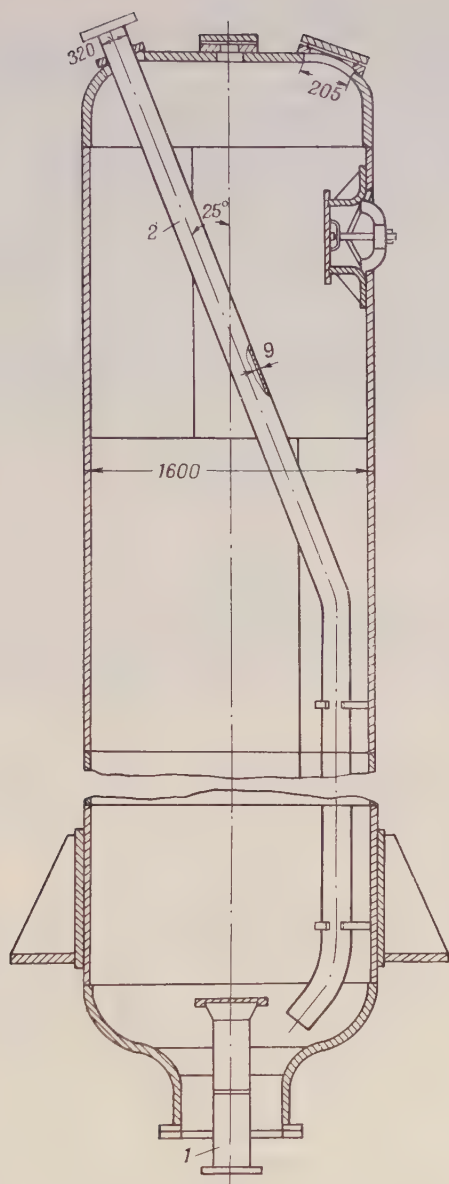


Fig. 172. Autoclave, or digester, heated with live steam

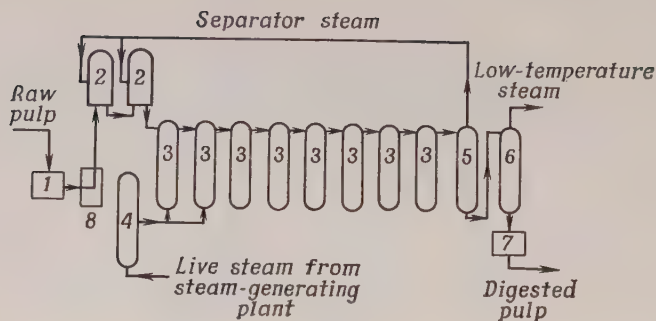


Fig. 173. Diagrammatic flow-sheet of continuous digestion:
 1—stirrer; 2—heaters; 3—autoclaves; 4—buffer vessel; 5—1st-stage separator; 6—2nd stage separator; 7—stirrer; 8—pump

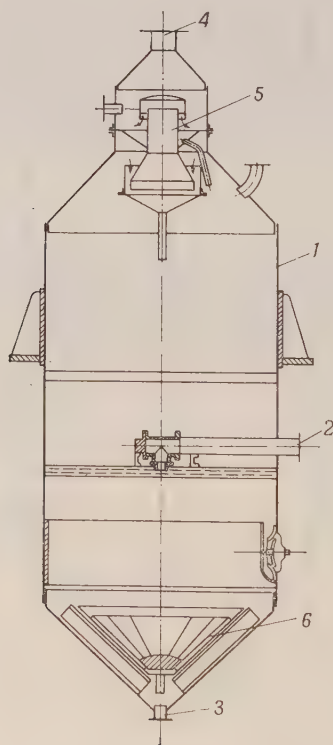


Fig. 174. Steam separator for digested liquor:
 1—shell; 2—liquor in; 3—liquor out; 4—steam out; 5—drip pot; 6—baffle

Live steam under a pressure of 25 to 30 atm is usually admitted into the first two autoclaves in order to raise the pulp to the desired temperature. The digesting treatment takes place as the pulp flows through the subsequent autoclaves. From the last autoclave the pulp is discharged into the first separator 5 where the pressure is brought down from 20 or 24 atm to 8 atm, and then into the second separator 6 where the pressure is further reduced to 1.5 atm.

The pulp enters the steam separator (Fig. 174) at a high velocity due to the pressure differential. As a protection against attrition by the pulp jet, the bottom of the separator has a baffle 6 of armour plate. In the evaporator, the pulp boils violently and its temperature drops. At the top of the evaporator there is a drip-pot 5 to catch the drops of liquor entrained by the steam.

The steam from the separators is utilised in the process. From the first-stage separator it goes to preheat the pulp in heat exchangers. The low-temperature steam from the second-stage separator is utilised to heat the water intended to wash the slime.

The variables of the digesting treatment (duration, temperature, liquid-to-solid ratio, fineness of ground bauxite, etc.) depend on the properties of the bauxite treated.

The rate at which bauxite dissolves in alkalis greatly depends on the mineralogical composition of the ore. The fineness of the bauxite required for successful digestion varies between 0.83 and 0.06 mm. The other variables are summarised in Table 47.

Table 47

**Suggested Variables of Digesting Treatment
for Bauxites**

Variables	Diaspore and boehmite	Gibbsite
Temperature, °C	205-250	105
Pressure, atm	15-35	1
Duration, h	2-2.5	1
Concentration of fresh NaOH, g/lit	300-320	200
Caustic ratio of recycled liquor	3.8-3.4	3.8-3.4
Lime addition, per cent	3-4	None

The recycled or return liquor (see Fig. 171) carries much sodium aluminate; its concentration is assessed in terms of the caustic ratio. The alkali in the aluminate liquor is classed into free (NaOH), aluminate (present as aluminate in the liquor), and carbonate (present as Na_2CO_3). The sum of the free and aluminate alkali is called caustic alkali and designated $\text{Na}_2\text{O}_{\text{caust}}$, and the sum of the

caustic and carbonate alkali is referred to as the total alkali ($\text{Na}_2\text{O}_{tot}$).

The caustic ratio is the molar ratio of the caustic alkali to the alumina in the liquor. For a liquor containing 300 grams per litre of caustic alkali and 145 grams per litre of alumina the caustic ratio will be:

$$\alpha_c = \frac{\text{Na}_2\text{O}_{caust}}{\text{Al}_2\text{O}_3} = \frac{300 \times 102}{145 \times 62} = 3.4$$

where 62 and 102 are the molecular weights of Na_2O and Al_2O_3 .

The digested liquor (including the residue of impurities) after it is cooled in separators is diluted with wash waters for better separation of the solids (known as "red mud") and removal of silicon (because the solubility of sodium-aluminium silicate in the aluminate liquor is reduced with decreasing concentration).

The diluted liquor is next run into a settling tank and allowed to settle so as to effect separation of the red mud from the sodium-aluminate solution. Ordinary thickeners such as described in the section on ore dressing are used as settling tanks.

Before it goes to waste, the red mud from thickeners is thoroughly and repeatedly washed. The overflow is put through filter-presses or leaf filters to obtain a sodium-aluminate liquor with a caustic ratio of about 1.7 : 1 containing about 120 grams of Al_2O_3 per litre. The sodium-aluminate liquor is next subjected to precipitation.

Precipitation is based on the property of sodium aluminate to decompose of itself, leaving aluminium hydroxide as a residue:



A plausible explanation of this behaviour is that alkali aluminates are salts produced by reactions between a weak metaaluminic acid (HAlO_2) with strong bases (such as NaOH). As will be recalled, such salts tend to hydrolyse.

As the reaction is reversible, the solution simultaneously contains undecomposed sodium aluminate, sodium hydroxide and aluminium hydroxide. The latter is apparently present in solution in the beginning and comes down as a crystalline residue afterwards.

It may be assumed that the sodium-aluminate liquor is decomposed in two stages: first, the aluminate liquor is hydrolysed, with particles of hydroxide forming crystallising nuclei, and then the crystals of hydroxide grow. The sodium-aluminate liquor in which decomposition has not started yet may be thought of as a solution in which either hydrolysis or crystal growth has not commenced yet, or both processes proceed so slowly that very little residue comes down.

The hydrolysis of the sodium-aluminate liquor may be retarded by increasing its caustic ratio, i.e., the concentration of free alkali.

A high caustic ratio and some other factors may shift the equilibrium towards the formation of sodium aluminate, which takes place when bauxite is digested in autoclaves at elevated temperature.

To sum up, apart from the caustic ratio, the stability of the sodium-aluminate liquor is affected by several other factors. Among other things, an increase in temperature increases the stability; an increase in liquor concentration acts in the same direction, as does the presence of some impurities (SiO_2 , organic matter).

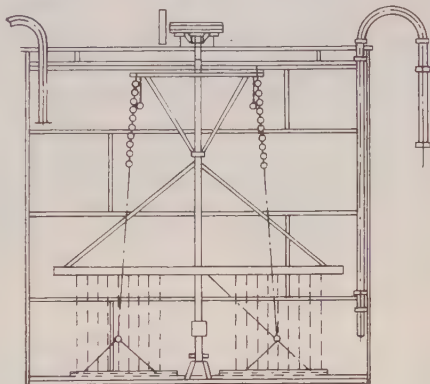


Fig. 175. Mechanically agitated precipitation (or decomposing) tank

Industrial practice is to speed up the decomposition of autoclave sodium-aluminate liquor by adding freshly prepared aluminium hydroxide in order to produce a multitude of crystallising nuclei throughout the liquor.

Precipitation is carried out in cylindrical tanks. The charge is stirred either by chain stirrers or by compressed air so as to equalise the concentration of the liquor around crystallising nuclei and to keep them suspended, thereby facilitating precipitation. Figs. 175 and 176 give a diagrammatic presentation of two types of precipitation (or decomposing) tanks. In the Soviet Union, use is predominantly made of tanks in which the charge is stirred by compressed air. Precipitation may be carried out either continuously in a series of 9 to 16 tanks connected by siphons, or intermittently in a single tank.

In the case of continuous operation, the head tank is filled with a sodium-aluminate liquor containing about 120 grams of Al_2O_3 per litre with a caustic ratio of about 1.7 : 1 and fresh sodium hydroxide as the seed, taking care that the seed contains 40 to 100 per cent more alumina than the liquor contains aluminium oxide (a seed ratio of 1.4-2.0 to 1).

To speed up decomposition, the charge is cooled to 60-65 C and the temperature is further brought down to 38-43 C as the precipita-

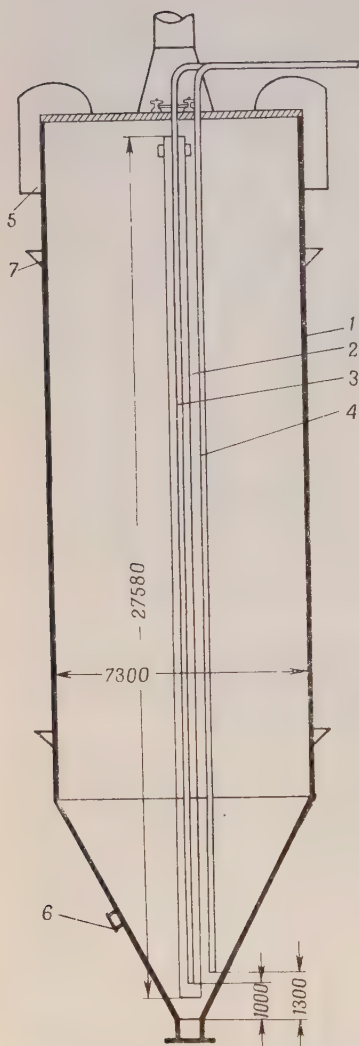


Fig. 176. Air-agitated precipitation (or decomposing) tank:
 1—shell; 2—airlift pipe; 3—central air pipe; 4—side air pipe; 5—air-cooling pocket; 6—inspection man-hole; 7—water-cooling ring

tion proceeds. For all the measures listed, aluminium hydroxide is precipitated over a period of time up to 100 hours. The precipitation is considered completed when the caustic ratio is 3.4-3.9 to 1.

The quality of the precipitated aluminium hydroxide depends on the fineness and purity of the residue. Too fine particles are undesirable, as they handicap the subsequent settling and washing of the hydroxide and also add to the losses of alumina during calcination and electrolysis. Too big pieces, on the other hand, are difficult to electrolyse.

After precipitation, the hydroxide is classified into fines which are returned to the process as the seed, and a coarse fraction which is thoroughly washed and filtered, yielding a product for calcination to alumina.

The purpose of calcination is to drive off all the water from the aluminium hydroxide and to produce practically unhygroscopic alumina.

As has been noted elsewhere, the decomposition of aluminium hydroxide is completed at 550°C. However, dehydration at this temperature produces gamma- Al_2O_3 which is fairly hygroscopic. In the temperature range 950-1200°C part of this modification changes to alpha-alumina.

Calcination is carried out in rotary kilns. A rotary kiln consists of a cylindrical jacket (50 to 150 m long and 2.5 to 5 m in diameter) made of riveted or welded steel plates lined with refractory firebrick. The steel jacket is surrounded by several wear-resisting steel tyres 30-60 cm wide by means of which it is rotated on friction roller bearings. These bearings are so adjusted that the jacket has an

inclination of 2 to 5 per cent with the horizontal (Fig. 177). The jacket is rotated at a speed of 1 or 2 rpm by an electric motor geared via a reduction gear to the girth gear on the jacket. The lower, or "hot", end of the jacket fits into a fire hood where nozzles squirt a liquid or a gaseous fuel. The upper end of the kiln enters a flue from which the products of combustion escape to the stack and the aluminium hydroxide is continuously charged into the kiln. Owing to the inclined jacket, the material is slowly moved downwards against the current of hot gases as the kiln is rotated. During its passage through the kiln, the material gives up its water slowly to become alumina as it reaches the hood. In the hood, the alumina flows by gravity down a chute at the bottom of the fire hood into a cooler.

In most cases, the cooler is similar in construction to the kiln. As distinct from the kiln, it is smaller in size and is lined with refractory firebrick to one-third of its length. The alumina is cooled by air drawn in through the cooler and by water sprinkled over the cooler on the outside (Fig. 178).

Calcined alumina is sent to manufacturers of aluminium by electrolytic processes.

The sodium-hydroxide liquor from the precipitating tanks has a caustic ratio of 3.4-3.9 to 1 and carries about 130 grams of Na_2O per litre. It is evaporated and concentrated for re-use in the treatment of raw bauxite.

The evaporation of the return liquor is complicated by the appearance of crystals of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. The sodium carbonate is formed by the reaction of sodium hydroxide with the carbonates in the bauxite and with the carbon dioxide of the atmosphere.

The residue of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is separated from the liquor in settling tanks and vacuum filters and is then treated with lime at 90-95°C in order to regenerate sodium hydroxide. As a result, aqueous sodium hydroxide and slime are formed according to the reaction:



They are separated by thickening and washing. The slime mainly consisting of CaCO_3 goes to waste. The solution obtained by the lime treatment is mixed with the strong liquor produced by evaporation and is re-used for the treatment of raw bauxite.

The Bayer process uses 2 to 2.5 tons of bauxite, 0.07 to 0.12 ton of sodium hydroxide, over 8 tons of steam and about 300 kWh of electricity to produce one ton of alumina. The loss of sodium hydroxide is made up with the fresh product bought on the market. The total recovery of Al_2O_3 from bauxite by the Bayer process is about 90 per cent.

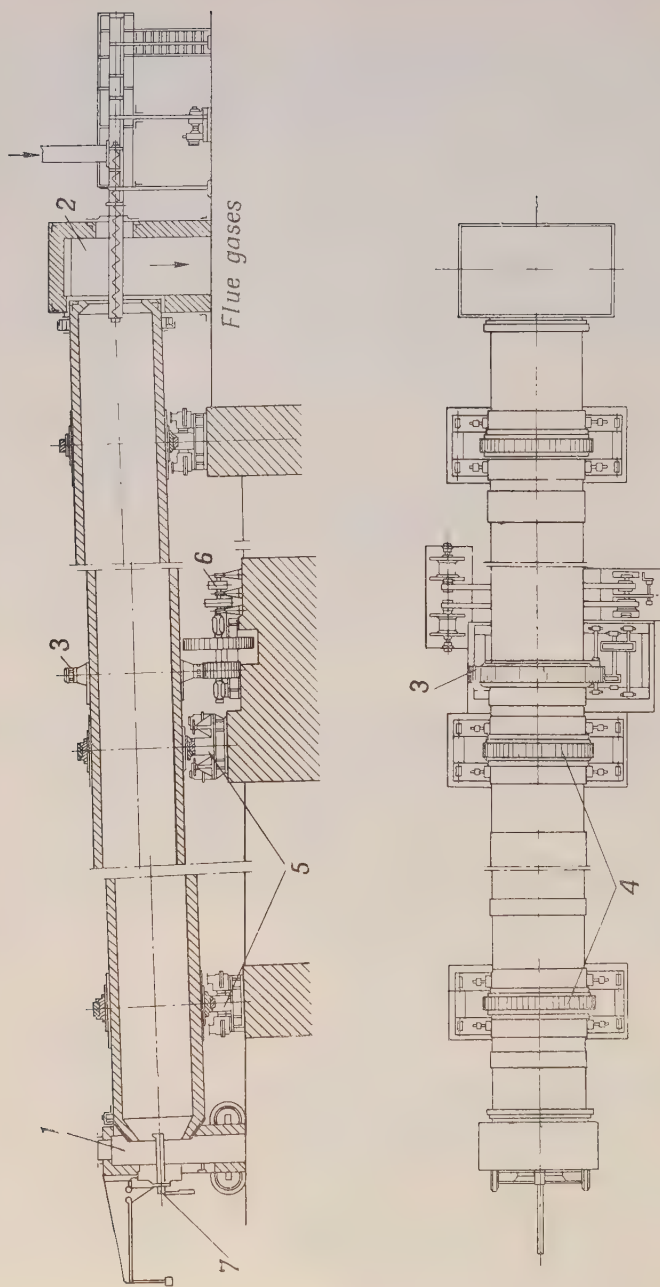


Fig. 177. Rotary kiln:

1—fire hood; 2—charging end; 3—girth gear; 4—supporting tyres; 5—supporting rollers; 6—reduction unit; 7—burner

A number of alumina factories handling bauxites easy to break down make up for losses of sodium hydroxide by adding cheap soda and lime to the process. The soda-lime reaction is usually combined with the grinding and lixiviation of the bauxite. Hence the name of this modification—the soda-lime process.

The Bayer process is the one most generally employed since it is economical and produces alumina of good quality. It should be

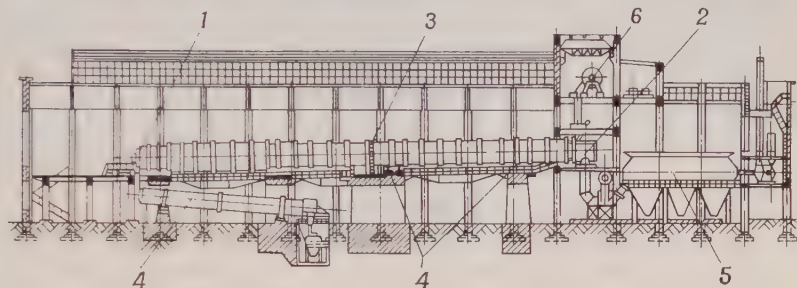


Fig. 178. Sectional view through an alumina-calcination plant:

1—fire hood; 2—stationary charging end; 3—rotary kiln jacket; 4—rotary cooler; 5—dust catchers; 6—drum filter

noted, however, that the Bayer process is best of all applicable to low-silicon bauxites, for every kilogram of SiO_2 present in the bauxite involves the loss of 0.85 kg of Al_2O_3 and 0.67 kg of NaOH . This is the reason why high-silica bauxites are treated by other processes. This purpose is served by the Deville-Pechiney (or Le Chatelier-Morin) process.

117. The Deville-Pechiney (or Le Chatelier-Morin) Process of Alumina Preparation

This process boils down to producing sodium aluminate at elevated temperature. The roasted mass is then lixiviated with water. The sodium-aluminate liquor thus obtained is decomposed by blowing with carbon dioxide, and the resulting aluminium hydroxide is calcined to alumina.

In a modification of the process, a wet bauxite charge is roasted. A simplified flow-sheet for the process is shown in Fig. 179. Bauxite and limestone are ground and mixed with the white slime, recycled sodium hydroxide, and a freshly prepared solution of sodium carbonate added to make up for its loss. The wet charge is then ground in a ball mill and transferred into a conditioning tank where it is continually stirred to prevent it from settling. When the conditioning tank is filled to capacity, its content is analysed and

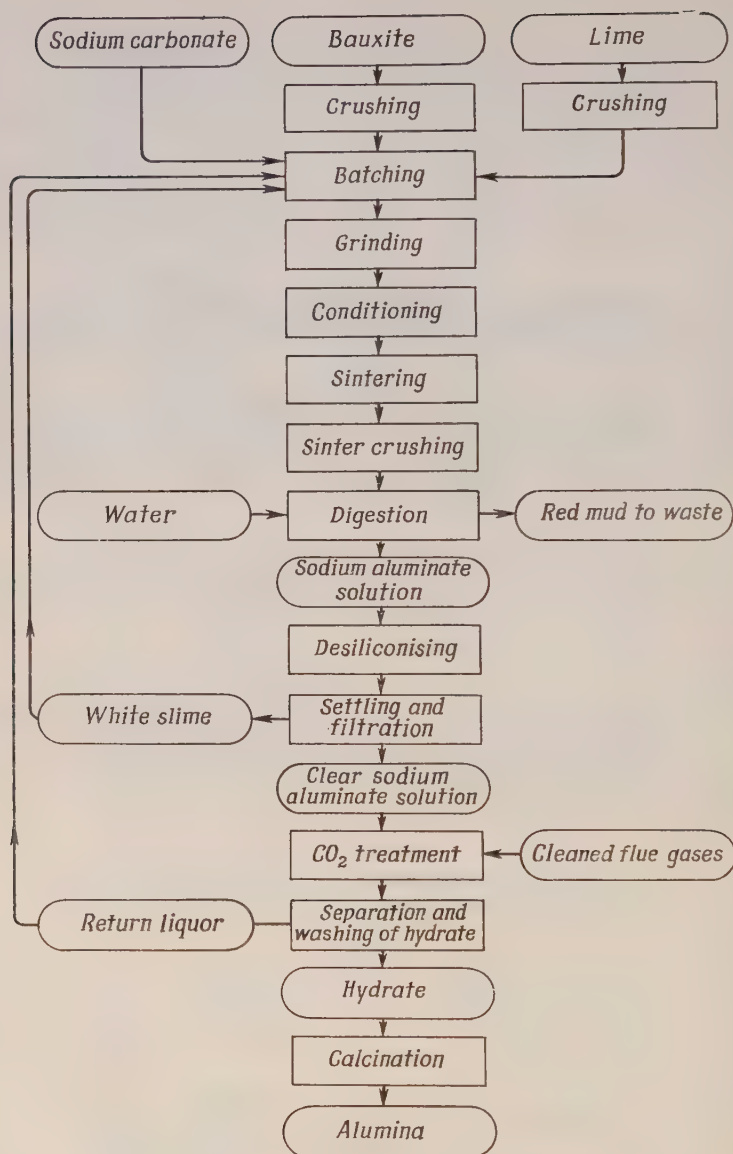
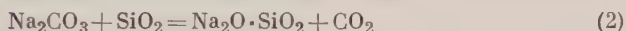
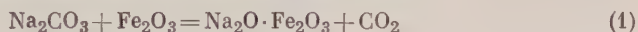


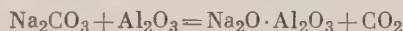
Fig. 179. Simplified flow-sheet for the Deville-Pechiney process of alumina preparation

the liquor from several conditioning tanks is mixed to the desired proportion, if necessary. The mixed liquor is next sintered. The purpose of sintering is to produce sodium aluminate soluble in water and to convert the silica of the charge to nearly insoluble calcium silicates.

To this end, the liquor is proportioned so that there is one gram-mole of Na_2CO_3 to every gram-mole of Al_2O_3 and Fe_2O_3 , and 2 gram-moles of CaCO_3 to one gram-mole of SiO_2 . The charge containing about 40 per cent moisture is forced by a nozzle into the "cold side" of a rotary kiln (see Fig. 177). Projected through the kiln, drops of the material dry and fall down to the lining of the kiln. Gradually picking up heat, the material moves into the hot zone of the kiln where the temperature is $1200\text{--}1300^\circ\text{C}$. As it grows hot, the material undergoes the following reactions:

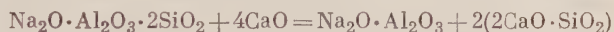
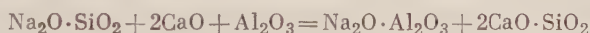


The sodium carbonate reacts with the ferric oxide and silica at a relatively low temperature. Simultaneously, the sodium carbonate reacts with the alumina:



The rate of this reaction, however, is considerably lower than that of reactions (1) and (2). At the same time, complex compounds may form, such as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, etc.

By the time the temperature reaches 900°C , no free sodium carbonate is left, and the products of reactions (1) and (2) react with the calcium oxide and alumina:



The sintering operation is also accompanied by other, more complicated reactions which produce the largest amounts of calcium aluminates ($\text{CaO} \cdot \text{Al}_2\text{O}_3$, etc.), calcium ferrites ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, etc.), and some other compounds.

Investigations have shown that heating to 1200°C causes the bulk of the aluminium oxide to form sodium aluminate. The sintering operation produces a lumpy, porous and slightly fused mass dark-grey in colour and flue gases.

The flue gases carry off with them much dust. Accordingly, they have to be thoroughly cleaned before they are utilised in the carbon-dioxide blow (see below). The dust is added to a fresh charge and returned to the process. Leaving the kiln, the sinter is cooled in rotary coolers and ground.

The ground material is then leached to dissolve the aluminates and remove into solution as much alumina and alkali as possible, taking care not to dissolve the other constituents. Leaching is done with water, diluted solutions of sodium carbonate or sodium aluminate.

Industrial practice uses three leaching methods: percolation of the leaching solution through the lumpy material, agitation leaching of the ground sinter with a solvent; and, more recently, continuous leaching of the lumpy sinter.

Percolation is carried out in diffusors (Fig. 180). A typical leaching plant will consist of 12 to 14 diffusors so connected that all of them may be operated in series or any of them brought out of the system at will, without upsetting the operation of the plant. Leaching is carried on in 9 to 11 tanks simultaneously. The solvent is fed into the "tail" diffusor, allowed to flow through all the other tanks and withdrawn as a strong sodium aluminate liquor from the "head" apparatus. In the meantime, one tank is being charged with the sinter, another is being emptied of the leached residue, and still another is being inspected and repaired. At regular intervals, the diffusor just charged with sinter is connected to the "head" apparatus, and the "tail" apparatus is disconnected for discharging.

This treatment produces a strong liquor with a concentration of 160 to 300 grams of Al_2O_3 per litre and requires no equipment for separating the mud. Unfortunately, some alumina is lost due to incomplete leaching, and the process as a whole involves a good deal of manual labour.

Agitation leaching is carried out in tanks fitted with stirring apparatus and may be conducted either continuously, with the pulp flowing by gravity through a series of tanks, or intermittently in a single tank.

The recovery of Al_2O_3 and Na_2O from the sinter is more complete with agitation leaching, but the resulting liquor carries but 120 to 140 grams of Al_2O_3 per litre. This necessitates the use of larger tanks, bigger electric motors and pumps, if the same alumina output is to be obtained from the weaker liquor. Furthermore, equipment has to be provided for separating the liquor from the residue and for washing the latter (thickeners, filters, stirrers, etc.). Putting it another way, agitation leaching involves greater capital outlays and maintenance expenses. Sometimes, the wet grinding of the sinter in ball mills is combined with the leaching operation—an arrangement which speeds up leaching and reduces the number of tanks.

To meet the requirements of the continuous leaching of the lumpy sinter, a new rotary apparatus has been developed and tested industrially in the Soviet Union. The apparatus (Fig. 181) consists of an

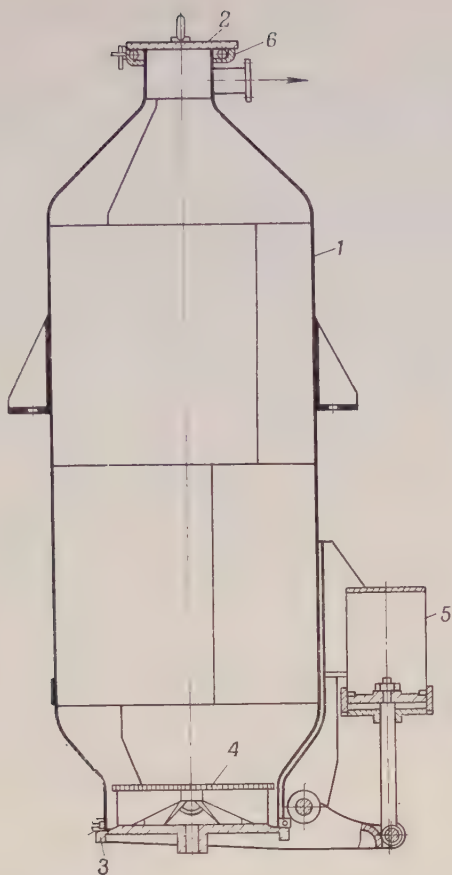


Fig. 180. Bottom-discharged diffuser for percolation leaching:

1—steel shell; 2—charging hole and lid; 3—discharge lid; 4—grill and net; 5—hydraulic actuator of discharge lid; 6—rubber-tube seal

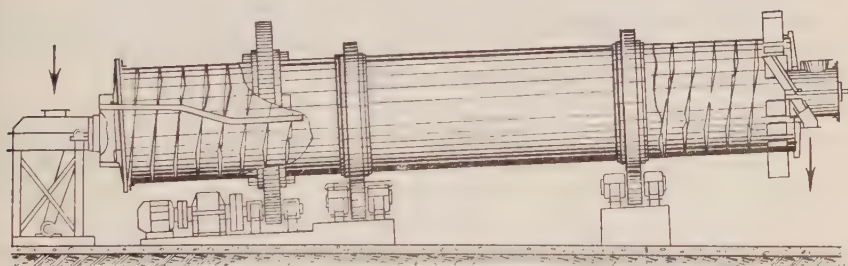
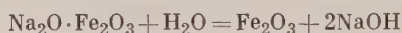


Fig 181. Rotary digester for roasted material

inclined jacket which houses a perforated helix. The sinter is fed at the lower end of the jacket and is moved upwards as the helix rotates. Water is admitted at the upper end and flows down the jacket by gravity. As it moves towards the lower end through the openings in the helix, it leaches the charge. The resulting sodium-aluminate liquor escapes at the lower end, and the mud is withdrawn from the upper end. This type of leaching equipment is being installed at new alumina plants in the Soviet Union.

The leaching of the sinter involves the following reactions. Sodium aluminate is dissolved in hot water. Then the sodium-aluminate solution may undergo hydrolysis, and so some alumina may be lost.

Sodium ferrite is hydrolysed in water according to the reaction:



The iron oxide remains in the residue, and the alkali is dissolved, thereby increasing the caustic ratio, and consequently, the stability of the sodium-aluminate liquor. This reaction proceeds at a slower rate than does the dissolution of sodium aluminate, and the danger of some sodium aluminate to be hydrolysed remains.

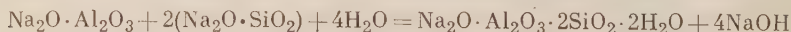
Calcium compounds do not practically dissolve in water; when attacked by alkaline solutions for a long time, however, they begin to decompose.

In addition to the sodium aluminate and sodium hydroxide, some silica also passes into solution as sodium silicates, which fact has an adverse effect on the whole process.

The recovery of alumina and alkali and also the amount of silica passing into solution all depend on the quality and fineness of the sinter, the nature and concentration of the leaching solution, temperature, the design of the equipment, the duration of the operation, and some other factors. The optimum conditions under which the greatest possible proportion of the values is extracted at the lowest possible cost can be found by trial and error.

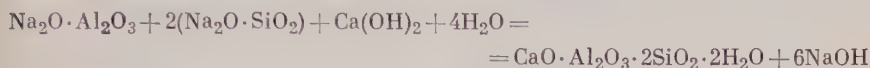
The sodium-aluminate liquor produced by leaching is then treated for the removal of the silica. The treatment consists in converting the dissolved silica into insoluble compounds.

This objective may be achieved by two methods. By the first method, the liquor is heated for a long time until poorly soluble sodium-aluminium silicate is formed which comes down as a white residue, according to the reaction:



By the other method, the liquor is heated in the presence of some lime. The removal of silica is more complete than by the first method

owing to the formation of poorly soluble calcium aluminium silicate (white slime):



In both cases, the removal of silica depends on the concentration of the sodium-aluminate liquor, the solubility of alumo-silicates increasing with increasing concentration of the liquor. As a precaution, therefore, strong sodium-aluminate liquors ought to be diluted prior to the removal of silica. The latter is facilitated by increasing the temperature and duration of the treatment which is usually conducted in a series of autoclaves heated with live steam at a temperature of 150°C for 2 to 4 hours.

In any case, some silica does remain in the liquor, and it is customary to assess the degree of silica removal by the silica ratio, i.e., the ratio (by weight) of the Al_2O_3 to the SiO_2 of the liquor. Obviously, the removal of silica is more complete with a greater ratio.

After the removal of silica, the sodium-aluminate liquor with a silica ratio of 300-500 : 1 and white slime are transferred from the autoclave into a thickener. After the separation of the white slime and clarification in filter-presses, the liquor is blown with carbon dioxide, while the white slime is returned to the sintering stage.

The blow with carbon dioxide (carbonation) serves to precipitate pure aluminium hydroxide from the liquor. The requisite CO_2 supplied by scrubbed flue gases reacts with the sodium hydroxide of the liquor according to the reaction:



As more sodium hydroxide is converted into sodium carbonate, the stability of the liquor decreases, and it decomposes of itself according to the reaction utilised in precipitation:



The sodium hydroxide produced by this reaction is again treated with carbon dioxide.

Thus, the decomposition of the liquor during the CO_2 blow is due to the hydrolysis of sodium aluminate. As distinct from ordinary precipitation, the CO_2 treatment proceeds at a high rate and to any degree of completeness. It takes 7 or 8 hours to carry the treatment to completion. Fig. 182 gives a chart of the treatment.

Special mention should be made of the behaviour of the residual silica during the CO_2 blow. Referring to the chart, the silica content of the liquor remains practically unchanged for several hours and sharply drops during the final period when little alumina is left in the liquor. For this reason, the usual practice is not to carry

the CO_2 treatment to completion, since otherwise the purity of the alumina may be impaired.

The sodium-aluminate liquor after incomplete CO_2 treatment may be either returned to the process or treated for the recovery of low-grade aluminium oxide. It is a good plan, after incomplete CO_2 treatment, to allow the liquor to decompose of itself, with the

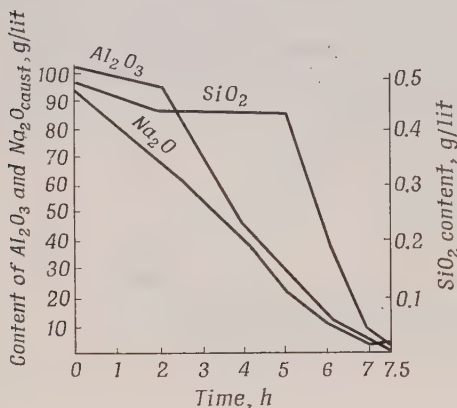


Fig. 182. Carbonation curves of sodium-aluminate liquor

gas supply shut off. Although this procedure takes more time, the aluminium hydroxide is of higher purity and in the form of large crystals, while the sodium-hydroxide liquor has a higher caustic ratio. The latter factor is important in that the presence of sodium hydroxide in the recycled liquor prevents hydrolysis of the sodium aluminate during leaching before the sodium ferrite decomposes, and also supplies some of the sodium hydroxide required, which is especially vital when low-iron bauxites are treated by the sintering process.

As in precipitation, CO_2 treatment should produce not only pure aluminium hydroxide but a product of the required fineness (crystals measuring about 60 microns in diameter). Too fine a precipitate will handicap the subsequent operations. Too coarse a product consisting of clusters usually contains much unwashable sodium carbonate, and the quality of the alumina will be impaired.

The gas withdrawn from sintering kilns contains 10 to 14 per cent CO_2 . The treatment is carried out in carbonisers—cylindrical tanks with chain stirrers (Fig. 183), at a temperature of 75 to 80°C. At lower temperatures, fine aluminium hydroxide is produced. After carbonation, the sodium hydroxide is separated from the aluminium hydroxide and is returned to the process, while the aluminium hydroxide is thoroughly washed and calcined to alumina exactly as in the Bayer process.

The sintering process, as developed in the Soviet Union, is applicable not only to high-silica bauxites but also to other aluminium ores, such as nephelines and some clays.

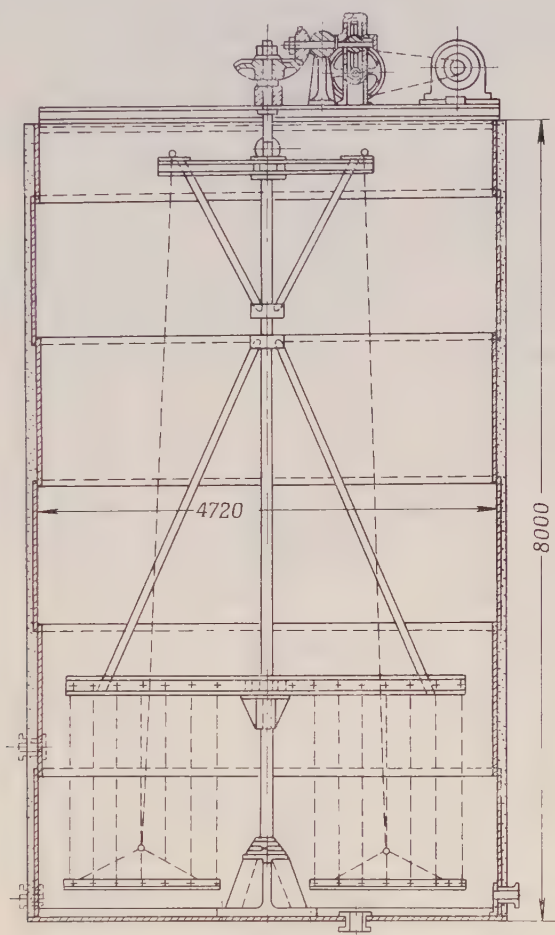


Fig. 183. Carboniser

Preparation of alumina from nepheline. The source material is the waste from the beneficiation of apatite-nepheline rock.

The basis of the process is sintering (Fig. 184), but the charge consists of two components: nepheline and limestone, for the concentrate contains enough Na_2O and K_2O to convert the alumina

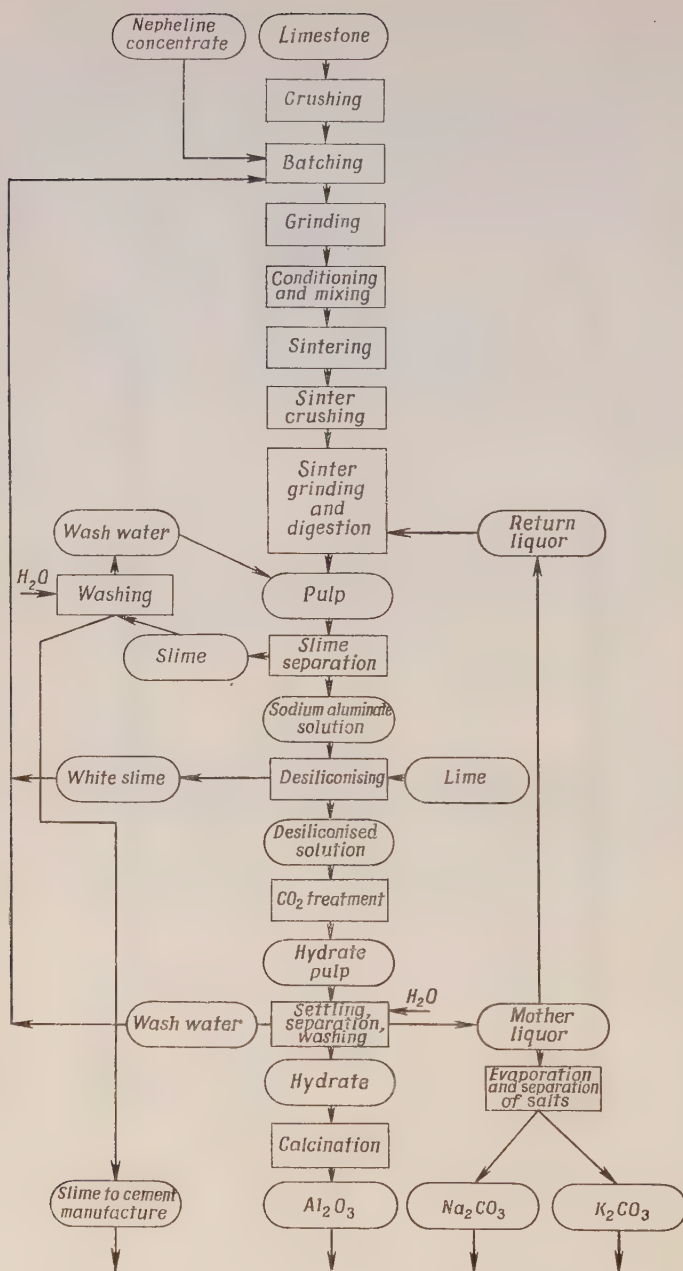


Fig. 184. Flow-sheet for nepheline treatment

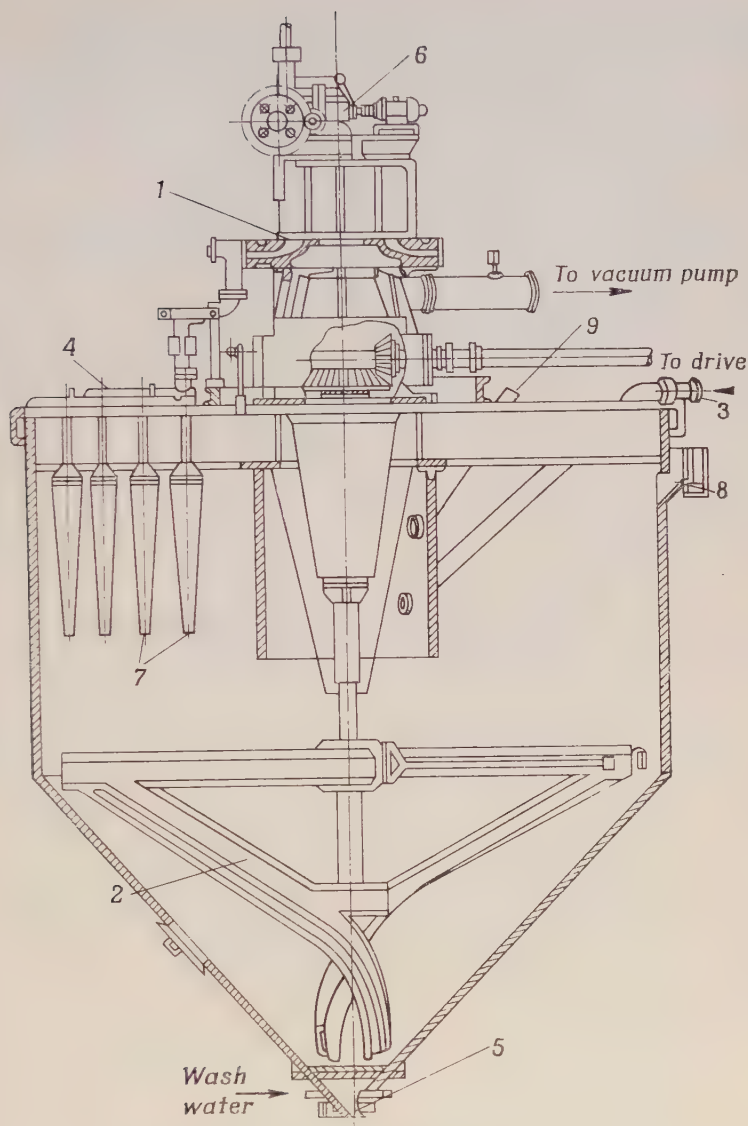
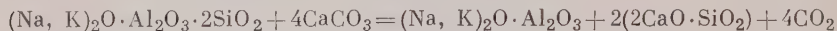


Fig. 185. Vacuum-thickener:

1—distributor head; 2—mixer; 3—charging pipe; 4—collector of the holder unit;
5—discharging cone; 6—distributor head drive; 7—holders; 8—overflow pipe; 9—air
exhaust pipe

into aluminates according to the reaction:



The limestone requires crushing and the nepheline concentrate regrinding. The charge is sintered in a rotary kiln at a temperature of 1250-1300°C.

The sintered mass is simultaneously ground and leached with the recycled sodium-hydroxide liquor in a ball mill. The sodium-hydroxide liquor is essential, since it imparts stability to the sodium-aluminate liquor during the leaching operation. The sodium carbonate present in the liquor decomposes part of the bicalcium silicate to produce additional sodium hydroxide. As a result, the sodium-aluminate liquor has a caustic ratio of 1.4 to 1 and carries 80 to 85 grams of Al_2O_3 per litre. The liquor is separated from the residue in thickening filters (Fig. 185), treated for the removal of silica, carbonated and calcined to alumina.

The residue left after the preparation of alumina from nepheline is made to cement; some of the liquor after carbonation goes to leach the sinter, and the remainder is utilised as a source of sodium carbonate and potash.

118. Other Processes of Alumina Preparation

Since 1945, several combinations of the Bayer and Deville-Pechiney processes have been developed. In them, high-silica bauxites are treated by the Bayer process with a high recovery of alumina, and the expensive sodium hydroxide lost in the process is replenished with the cheap soda ash.

In the *parallel* modification of the combination process low-silica bauxite is treated by the Bayer method and a small proportion of the bauxite is treated by the Deville-Pechiney process, with the loss of sodium hydroxide being covered up by sodium carbonate necessary for sintering.

The sodium aluminate from the sintering step is treated for the removal of silica and mixed with the liquor from the Bayer step, and the mixture is precipitated jointly.

In the *series* modification, developed by a research team under Masel (U.S.S.R.) in 1934 (Fig. 186), high-silica bauxites are treated by the Bayer process. The resulting red mud high in aluminium oxide and sodium hydroxide is roasted with sodium carbonate and limestone. The calcine is leached, giving a sodium aluminate liquor which is mixed with the liquor from the main process and precipitated.

When this process is applied to bauxites containing up to 14 per cent SiO_2 , the recovery of alumina is as high as 96 per cent; the

loss of the alkali is made up with sodium carbonate alone, and the caustic treatment of the recycled monohydrate of sodium carbonate may be dispensed with.

The alumina preparation by the Kuznetsov-Zhukovsky process. In 1915, Kuznetsov and Zhukovsky of Russia took out a patent for

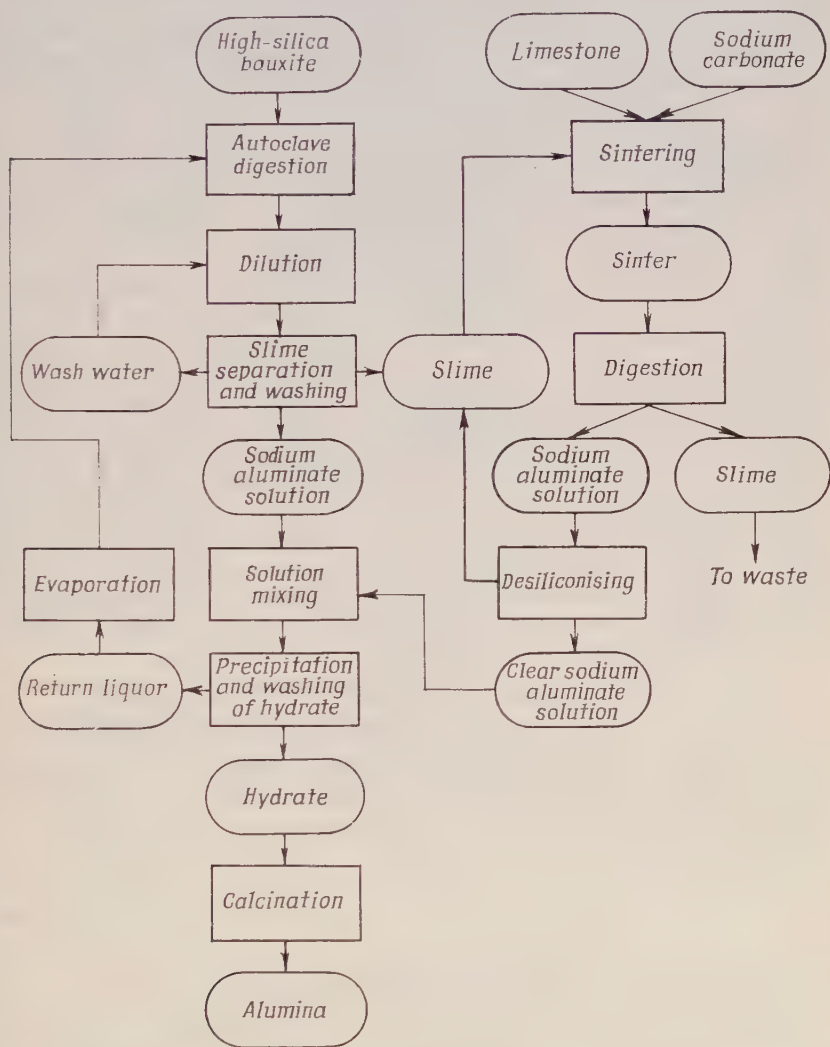


Fig. 186. Simplified flow-sheet for the preparation of alumina

a process for the preparation of alumina from the slags of the reduction smelting of aluminium ore with alkali-earth oxides.

By their process, bauxite, lime and coke are smelted in powerful electric furnaces. The complex reactions that take place in the furnace produce two liquid layers: ferro-silicon and an aluminous slag mainly consisting of calcium aluminates ($\text{CaO} \cdot \text{Al}_2\text{O}_3$, and the like) and some bicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$). The slag and the ferro-silicon are tapped at regular intervals. Upon solidification, the slag easily comes off the ferro-silicon. In cooling, the slag breaks to pieces owing to the presence of $2\text{CaO} \cdot \text{SiO}_2$ which changes from the beta- into the gamma-modification at 675°C and expands by 10 per cent. This appreciably simplifies the subsequent grinding of the slag.

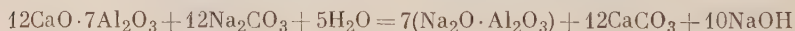
The ground slag is leached with a sodium carbonate solution, giving sodium aluminates. The liquor thus produced is treated much as the liquor of the roasted bauxite.

The process has a modification in which calcium aluminates are produced from high-iron bauxites in blast furnaces. This modification is promising in more than one respect.

The preparation of alumina from clays and marls. A more recent addition to alumina technology is its preparation from clays and marls (natural mixtures of clay and limestone).

The charge consisting of clay and limestone (or simply marl) is roasted in a rotary kiln at 1400°C . The roasted product contains 16-20 per cent Al_2O_3 , 58-62 per cent CaO and 20-25 per cent SiO_2 . Owing to the presence of much bicalcium silicate, it readily goes to pieces, like the slag in the Kuznetsov-Zhukovsky process.

The ground material is leached with the recycled sodium carbonate liquor. The principal reactions of the treatment may be presented as follows:



Next the mud is separated, the liquor treated for the removal of the silicon, and the remaining solution blown with carbon dioxide. The product is the hydrate of aluminium oxide which is calcined as usual.

The mud which has a composition close to that of the residue in the nepheline process is leached and sent for cement manufacture.

119. The Preparation of Cryolite

Molten cryolite with additions of some other fluorides is at present the chief and indispensable constituent of the electrolytic bath where it dissolves the alumina.

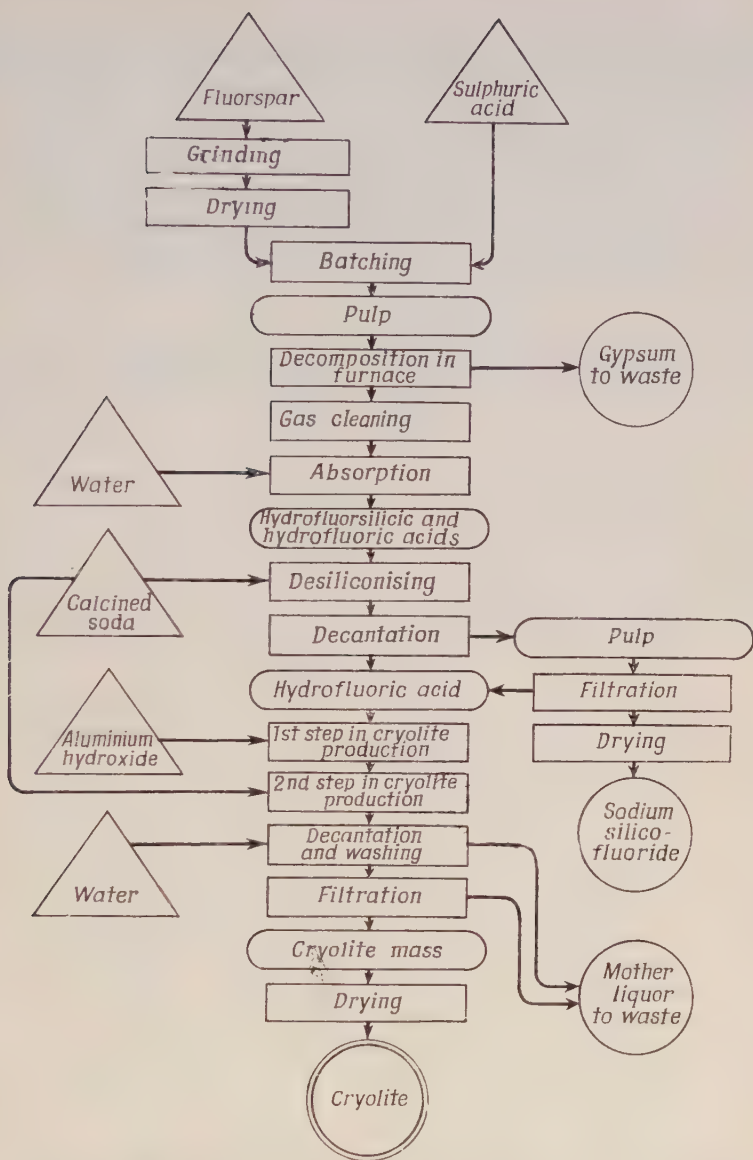
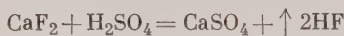


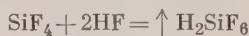
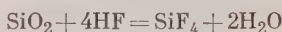
Fig. 187. Flow-sheet for the acid process of cryolite production

Cryolite occurs in nature, but there is only one commercial source of cryolite in south Greenland. The scarcity of natural cryolite has spurred the production of artificial cryolite, AlF_3 and NaF from fluorspar in many countries.

One of the processes for the production of artificial cryolite boils down to the following (Fig. 187). Natural fluorspar is concentrated to 96 per cent CaF_2 . The concentrate is mixed with strong sulphuric acid and the mixture is heated to 200°C in a rotary kiln. The treatment produces hydrogen fluoride and calcium sulphate according to the reaction:



At the same time hydrogen silicofluoride is formed:

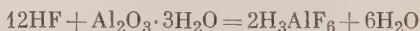


The last reaction usually takes place outside the kiln (in the flues and towers). The gaseous products of the reaction are absorbed by water in towers, giving a solution of hydrofluoric acid with an admixture of hydrofluosilicic acid.

The addition of sodium carbonate to the mixture throws down poorly soluble sodium silicofluoride:



Then the combining amount of aluminium hydroxide is dissolved in the purified hydrofluoric acid:



The hydroalumofluoric acid thus obtained is neutralised in the same tank with sodium carbonate, and nearly insoluble cryolite appears in the residue:



The cryolite is separated from the liquor, washed and dried at 140 to 160°C .

Other fluorides are made by completely neutralising the hydrofluoric acid with either the hydrate of aluminium oxide (if AlF_3 is to be obtained) or with sodium carbonate (to produce NaF).

The acid process of cryolite preparation suffers from serious drawbacks, such as high toxicity (HF and H_2SiF_6 are poisonous gases), expensive acid-proof apparatus, and low recovery of the fluorine into cryolite. Several other processes have been developed in the U.S.S.R. for the production of cryolite, but none of them has attained a commercial status yet. In one of them fluorspar is fused

with potash and amorphous silica (tripoli, etc). The fused material containing easily soluble KF is leached without difficulty, and the filtrate is treated with a sodium carbonate solution to precipitate crystals of sodium fluoride. These crystals are then added to a sodium aluminate liquor, and sodium cryolite is precipitated. This process may be carried out in ordinary steel or cast-iron apparatus. The reactions involved in the process do not produce any fumes of hydrofluoric acid, and there is no danger to attending personnel.

120. The Manufacture of Carbon Electrodes and Anode Material

The production of aluminium by the electrolytic decomposition of alumina involves the use of the following carbon products:

(a) blocks usually measuring 40 cm by 40 cm by 55 cm, to line the bottom of the electrolytic cell and to serve, at the same time, as the cathode;

(b) liquid or solid anode material to make self-baking continuous anodes;

(c) different sizes of slabs to line the side walls of the cell.

The source materials for these products must carry very little ash, since it would enter the electrolyte and contaminate the aluminium.

The baked carbon products must be sufficiently strong (with a compressive strength of 250 to 350 kg/sq cm) and dense (not over 25 per cent of voids).

Two classes of source materials go to make electrodes: solid carbonaceous materials which serve as the basis of electrodes, and various binding agents which hold the core material together.

The solid ingredient may be high-grade anthracite, petroleum or pitch coke low in ash (0.3 to 0.4 per cent).

The binder is usually pitch, an intermediate product of the distillation of coal tar, with a softening point of 45 to 85°C.

Fig. 188 shows a flow-sheet for the manufacture of carbon products. Anthracite and petroleum or pitch coke are crushed separately to 30-50 mm and calcined in rotary kilns or retort furnaces. The purpose of calcination is to reduce the content of volatile matter to not over 0.15 or 0.2 per cent and to make the material more inert, compact, strong and electroconductive. These changes are brought about by heating the charge to 1300°C in the absence of air. The calcined material is then ground, screened and sent for proportioning. The proportioning is done by trial and error, after which the material is mixed with the molten binder. This is done in paddle-type kneading machines at a temperature of 90 to 120°C. Leaving the kneading machine, the mix is formed to shape under a pressure of 250 to 400 kg/sq cm. Too high a pressure may crush the solid particles unduly, while with too low a pressure the products may

be weak. The shapes are either pressed in moulds or extruded through a die (Fig. 189).

The green shapes are not yet sufficiently strong or electroconductive. To make them such, they are baked at 1400°C in box or tunnel kilns in the absence of air.

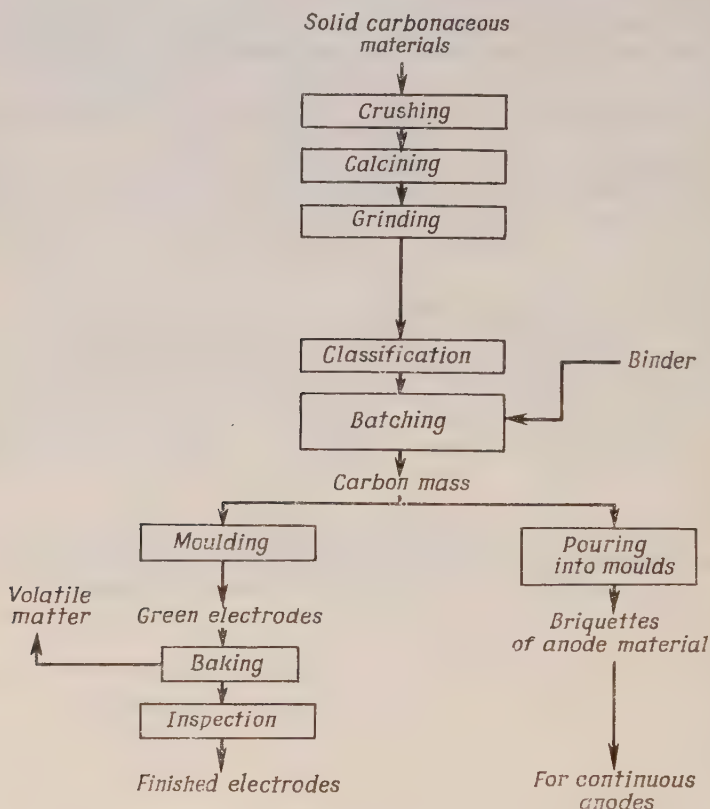


Fig. 188. Flow-sheet for the manufacture of carbon shapes and electrodes

During baking, the binder is coked, and the material becomes hard and strong and of increased electrical conductivity. This important operation requires that the temperature be raised gradually according to a schedule and usually lasts up to 200 hours. If the baked shapes are not to crack, their cooling must also be slow.

Where continuous anodes are employed, the forming and baking operations are omitted. The charge for continuous anodes carries greater amounts of binding agents and no anthracite.

Some manufacturers employ graphitised electrodes which have higher electrical and thermal conductivities in comparison with carbon electrodes and resist the attack of chlorine and oxygen

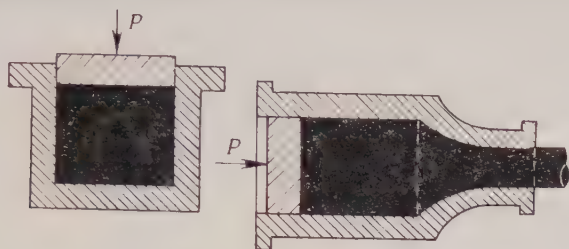


Fig. 189. Diagram of moulds for carbon shapes and electrodes

more efficiently. Graphitisation is conducted by heating baked carbon electrodes in resistance furnaces at about 2500°C for 60 to 75 hours in the absence of air.

Chapter XVII

THE PRODUCTION OF METALLIC ALUMINIUM

121. The Composition and Properties of the Bath

Aluminium oxide cannot be reduced to metallic aluminium by carbon smelting because the metal will again react with the carbon to form aluminium carbide, Al_4C_3 . Nor can aluminium be obtained by the electrolytic decomposition of an aqueous solution of its salts, for only hydrogen will evolve at the cathode. This is the reason why metallic aluminium is at the present time produced commercially by the electrolysis of alumina in a liquid bath of cryolite. The process is carried out in an aluminium-reduction cell shown diagrammatically in Fig. 190. The cell consists of a steel shell 1 set up on a substantial foundation and a carbon lining 2. The space within the lining is usually about a half-metre deep. Embedded in the cell bottom are steel rods 3 for the cathode connection. Several carbon

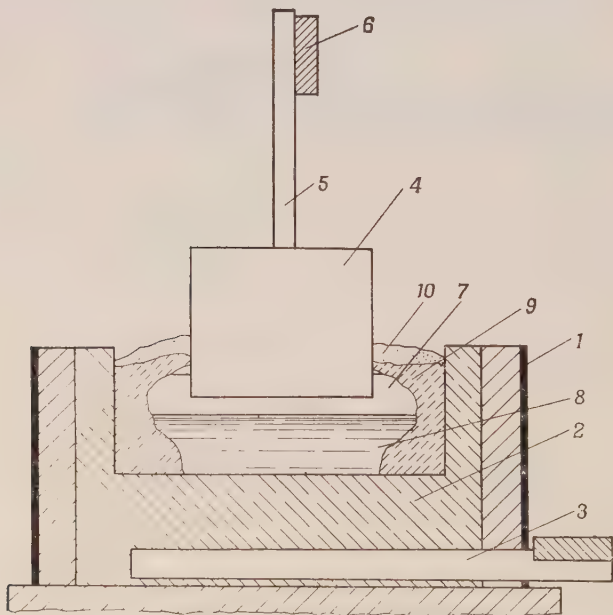


Fig. 190. Diagram of an aluminium-reduction cell

blocks 4 suspended from above serve as anodes. Current to the anodes is supplied by metal rods 5 and busbars 6. The anodes are partly dipped in the liquid bath of cryolite 7. Passing through the electrolyte, direct current maintains it in the liquid state and brings about the electrolytic decomposition of the alumina. The metallic aluminium collects on the cell bottom 8 which serves as the cathode. The oxygen evolving at the anodes oxidises the carbon of the anodes to CO and CO₂. The anodes are gradually lowered as they wear away. In operation, the cryolite bath forms a solid crust 9 on the walls and over the bath. To prevent undue loss of heat by radiation, alumina 10 is spread over the crust and when additional alumina is required in the bath the top crust is broken, the alumina pushed down and stirred in, and more alumina spread on the crust.

In practice, various bath compositions are employed. The main criterion of the quality of a bath is its molar ratio of NaF to AlF₃, known as the cryolite ratio. For pure cryolite it is 3 : 1. The commercial process uses so-called acidic baths with a cryolite ratio of 2.7-2.3 to 1. If too acidic, the bath will be excessively volatile and dissolve alumina less efficiently. Baths with a cryolite ratio of over 3 : 1 are unacceptable for the reason that sodium may deposit on the cathode owing to the increased concentration of sodium ions.

The cryolite ratio also has a decisive effect on the fusibility of the electrolyte. As will be seen from the diagram in Fig. 191, the system NaF-AlF₃, investigated by Fedotyev and Ilyinsky, has the highest melting point when its content of AlF₃ is 25 per cent (molar), which corresponds to pure cryolite. Referring to the system Na₃AlF₆-Al₂O₃ (Fig. 192), also investigated by Fedotyev and Ilyinsky, it will be noted that the melting point of the cryolite-alumina mixture steadily drops as the alumina content rises to 15 per cent. When more than 15 per cent alumina is present in the electrolyte, its melting point sharply rises. At 20 per cent alumina the melting point is 1000°C. In practice, however, the alumina content of the bath seldom exceeds 8 per cent.

Some manufacturers add fluorides to the bath. Most often use is made of calcium fluoride which reduces the melting point of the bath. This reduction in melting point has a favourable effect on the electrolysis. On the other hand, the addition of CaF₂ slows down the dissolution of alumina in fused cryolite and somewhat impairs its electrical conductivity. In the opinion of Belayev, MgF₂ is more attractive as an addition than CaF₂ as it brings down the melting point of the electrolyte more than CaF₂ does and also reduces its specific gravity. The latter property is important for the following reason. At 18°C the specific gravity of metallic aluminium is 2.7 and that of cryolite is 2.95. At the temperature of electrolysis, however, molten aluminium is heavier than the electrolyte, especially

if it carries much dissolved alumina. At 1000°C, for example, the specific gravity of aluminium is 2.3 and that of the cryolite-alumina mixture at 10 per cent alumina is 2.03. As a result, the aluminium sinks to the bottom. Should the bath be excessively cooled, the aluminium will float to the surface and oxidise, also short-circuiting the current and upsetting the operation in general.

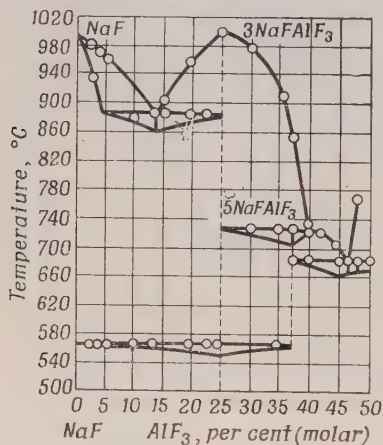


Fig. 191. Fusibility diagram of the system NaF-AlF_3 (after Fedotyev and Ilyinsky)

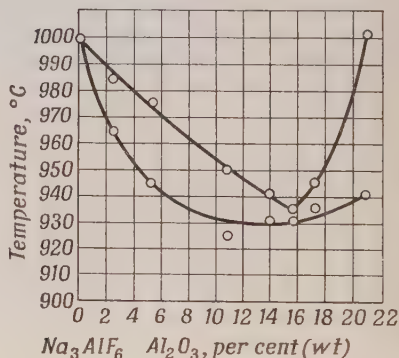
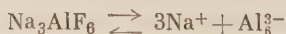


Fig. 192. Fusibility diagram of the system $\text{Na}_3\text{AlF}_6\text{-Al}_2\text{O}_3$ (after Fedotyev and Ilyinsky)

The electrical conductivity of the electrolyte is also important for the uninterrupted flow of the process. According to Batashev, at the composition 90 : 10 cryolite-alumina, the resistivity at 1000°C is 0.37 ohm-cm. Measurements in commercial baths have, however, produced higher figures. The explanation of the difference apparently comes from the presence of the impurities coal, carbides, etc., in the bath. For engineering purposes, the resistivity of the bath is assumed to be 0.5 to 0.55 ohm-cm. This is quite enough for the current passing through the electrolyte to dissipate as much heat as is necessary for maintaining the normal temperature of the process (about 950°C).

Speaking of the theoretical aspect of the process, there exist conflicting opinions as to which ions and to what extent carry current in the bath. The majority of Soviet investigators stick to the theory originally set forth by Fedotyev in 1923-32 and later expended by Mashovets, Abramov and others. According to this theory, molten cryolite, being a good conductor of current, dissociates into ions:



This agrees well with the crystal structure of cryolite (Fig. 193) which is basically octahedral with an aluminium ion in the centre and six fluorine ions at the corners. As liquids differ little in structure from the respective solids at near melting point, molten cryolite must contain "fragments" of its lattice, i.e., ions AlF_6^{3-} .

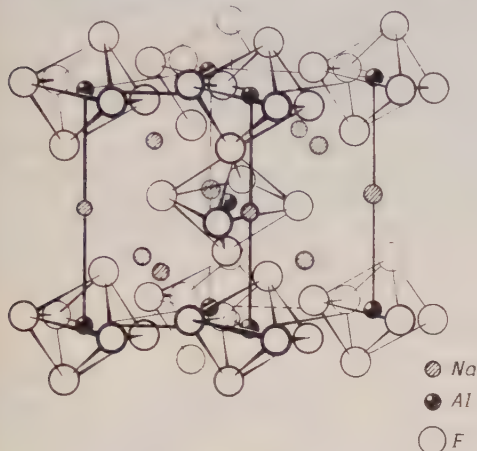


Fig. 193. Crystal structure of cryolite

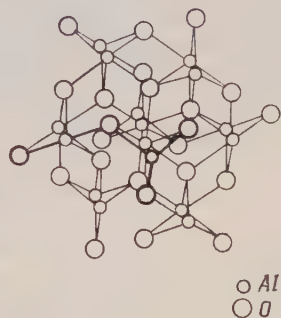


Fig. 194. Crystal structure of corundum

The alumina dissolved in fused cryolite dissociates into ions of aluminium and oxygen-bearing ions. According to Fedotyev, the following reaction is most probable:



Other investigators take a different view on the dissociation of alumina in molten cryolite. In Mashovets' opinion, oxygen is present in the bath as ions AlO_2^- . Pazukhin believes that the dissociation produces ions $\text{AlF}_5\text{O}^{4-}$ and ions O^{2-} . Guskov, Belayev and some others hold that the ions present in the molten cryolite-alumina bath include ions O^{2-} and Al^{3+} .

The mechanism of electrolysis may be pictured as follows. Near melting point the cryolite will consist of ions Na^+ and AlF_6^{3-} , since the ion bonds between the sodium and fluorine in the lattice are weaker than between the aluminium and fluorine. This, however, does not exclude the possibility of the crystal structure further breaking up into ions Al^{3+} and F^- .

As it dissolves in molten cryolite, alumina may break up into ions Al^{3+} and O^{2-} which make up its crystal structure (Fig. 194). It is also likely that the ion of oxygen which is of small size and

has a relatively large charge will combine with some other ions to form a complex oxygen-bearing ion (such as AlO_2^- or even $\text{AlF}_5\text{O}^{4-}$).

Thus, the bath may be assumed to consist of ions Al^{3+} , Na^+ , F^- and O^{2-} which move about continuously and may collide to form complex ions AlF_6^{3-} , AlO_2^- and, perhaps, some other. All of these ions carry current, though not in equal amounts, since it varies with their concentration and mobility.

Not all of these ions will discharge at the electrodes, but only those which have appropriate electrode potentials. The ion Al^{3+} will discharge at the cathode, and O^{2-} at the anode.

The oxygen evolving at the anode reacts with its carbon to form carbon monoxide which burns to carbon dioxide with a blue flame above the crust on escape into the atmosphere.

To sum up, the electrolytic action boils down to the production of Al and depletion of Al_2O_3 .

122. The Anode Effect

As the electrolysis proceeds, the alumina content of the bath becomes gradually exhausted. When it reaches about 1 per cent, what is known as the anode effect takes place in a normally operating reduction cell. Outwardly, it manifests itself as a jump from a normal voltage of 4.3 or 4.5 V to 20-40 V, which is indicated by the pilot lamp. Where the anode comes in contact with the electrolyte, small arcs strike, producing a hissing sound; the bath is heated, and some of its fluorine vaporises. The normal working of the cell is restored by adding a fresh charge of alumina from top of the crust. This should be done periodically, while keeping the alumina content at not over 8 per cent.

The anode effect is a very important factor in the electrolytic process. On the one hand, it indicates when a fresh charge of alumina should be added and whether the cell operates normally. In the case of normal cell operation, the sharp voltage jumps will recur at equal time intervals depending on the amount of alumina added to the bath and the value of current used. If the anode effect recurs irregularly and the voltage rises slowly or pulsates, the cell requires special measures.

On the other hand, the anode effect has a detrimental influence on the process in that it increases the consumption of power, fluorides and anodes and hampers operation of d.c. sources. For this reason, not more than one voltage jump is allowed to take place for 1 to 3 minutes during a day.

The anode effect has interested many investigators who have advanced quite a number of different views on its nature. A fundamental study into the nature of the anode effect has been conducted

by Belayev, Kuzmin and co-workers at the Kalinin Institute of Non-ferrous Metals and Gold in Moscow.

According to them, the anode effect occurs not only in the cryolite-alumina bath using carbon electrodes (as some investigators believe) but also during the electrolysis of any molten salt baths using any anodes.

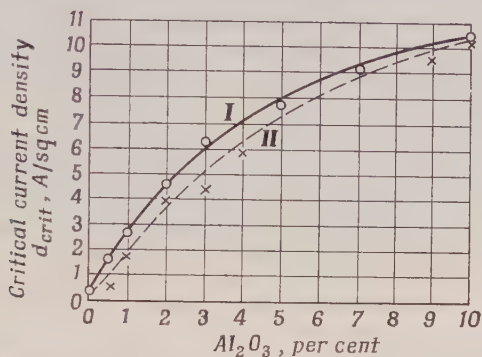


Fig. 195. Critical current density related to Al_2O_3 content in cryolite-alumina baths:

I—after Belayev and Kuzmin; II—after Karpachev, Dolgov and Konchinsky

It occurs when the current at the anode exceeds critical density. The value of critical density and, consequently, the occurrence of the anode effect depend on the character of the molten salt, the amount of oxides dissolved in it, the material of anodes, and the temperature of the melt. For molten chlorides, for example, the critical density of current will be higher than for fluorides, and especially when oxides are dissolved in the bath.

Fig. 195 shows the critical density of current in cryolite-alumina baths as a function of their Al_2O_3 content. Referring to the diagram, the critical density of current increases and the probability of the anode effect taking place decreases with increasing Al_2O_3 content. As commercial cells operate on a current density of 0.7 to 1.2 A/sq cm it may be inferred from the diagram in Fig. 195 that the anode effect will take place when the alumina content in the bath has dropped to 0.3-0.5 per cent.

In the light of Soviet studies, the mechanism of the anode effect may be thought of as follows: when the bath contains enough alumina, the molten electrolyte efficiently adheres to the anode surface and washes off the gas bubbles evolving on it (Fig. 196a). As the alumina content of the bath decreases, the electrolyte gradually ceases to wet the anode (Fig. 196b), and the gas bubbles are free to accumulate there, increasing the resistance to the current

at the interface between the anode and the electrolyte. Where the gas film is temporarily broken, electric arcs strike. An addition of

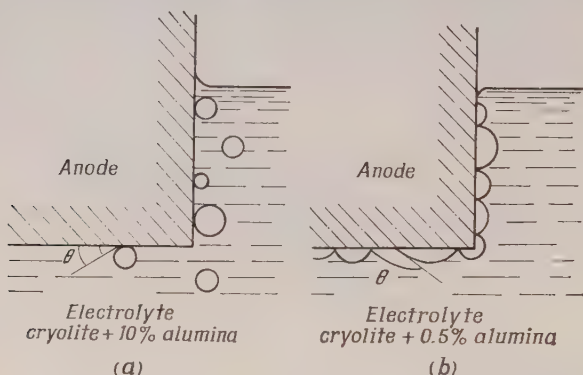


Fig. 196. Gaseous film formation at anodes:
(a) normal electrolysis; (b) anode effect

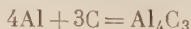
fresh alumina restores the wetting ability of the electrolyte, the gas film is removed from the anode, and the voltage across the cell returns to normal.

123. Minor Effects at the Cathode and in the Electrolyte

The electrolytic production of aluminium is accompanied by some minor effects which may result in the loss of aluminium, increased power consumption, impaired metal quality, changes in bath composition, etc. The most important among them are the dissolution of some aluminium, the formation of aluminium carbide, and the absorption of electrolyte by the cell lining.

The dissolution of aluminium in the electrolyte. Little metallic aluminium dissolves in the molten cryolite bath (in amount up to 0.1 per cent). As it spreads throughout the bath, however, it reaches the surface of the cell to be oxidised by the oxygen of the atmosphere, or comes in contact with the gases at the anodes to form Al_2O_3 , thereby causing more metal to dissolve in the electrolyte. The dissolution and oxidation of aluminium in the bath increase with decreasing electrode spacing and increasing temperature. It is good practice, therefore, to run the cell at the lowest practical temperature and optimum electrode spacing.

The formation of aluminium carbide. When the cell is run at an excessively high temperature, aluminium interacts with the carbon of the bath to form aluminium carbide:

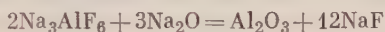


Favourable conditions for the formation of aluminium carbide arise when the crust on the sides and bottom of the cell melts to expose the carbon lining. Then the aluminium ions will discharge immediately on the carbon, and the aluminium atoms will react with the carbon to form aluminium carbide. Aluminium carbide is a refractory material of high specific gravity and low electrical conductivity; it forms on the cell bottom under the molten aluminium and also in the body of the electrolyte, thereby introducing an additional resistance to current. Also aluminium may find its way into the pores and cracks of the carbon lining and react with the carbon to produce bright-yellow crystals of carbide.

Changes in bath composition. With time the bath changes its composition variously. Observations have shown that during the first months of operation, the bath loses much of its sodium fluoride and becomes acidic. In cells operating over a year, the bath loses some of its aluminium fluoride and becomes alkaline.

Loss of aluminium fluoride is possible due to its volatilisation, especially during an anode effect, since the pressure of AlF_3 vapours at the working temperature is about 7 mm Hg.

Furthermore, the cryolite may react with the impurities SiO_2 , Na_2O and H_2O which may find their way into the bath with alumina and fluorides. The Na_2O remaining in the alumina due to the poor washing of the hydrate may decompose the cryolite according to the reaction



SiO_2 may be added to the bath as an impurity of both the alumina and cryolite. Part of it may decompose to contaminate the aluminium with silicon, while another part may react with the cryolite according to the reaction



giving volatile silicon tetrafluoride and breaking up complex ions of fluorine and aluminium (such as AlF_6^{3-}).

Normally, well-heated products are added to the bath, and water vapour may only form if the alumina contains some aluminium hydroxide. If so, the following reaction may take place:



All of these reactions produce an excess of sodium fluoride in the bath.

The absorption of electrolyte by the lining. Belayev and others at the Kalinin Institute of Non-ferrous Metals and Gold have shown that sodium fluoride adheres to carbon materials much better than does cryolite or aluminium fluoride. Therefore, some of the sodium

fluoride produced by the dissociation of the cryolite in the bath may be picked up by the carbon lining and cathode of a new cell, thereby upsetting the cryolite ratio. Examinations of the bottom blocks of old cells have borne this out. During the service life of a cell the density of the carbon blocks rises from 1.6 g/cu cm to 2.5 g/cu cm, and the material absorbed by the lining contains 70 to 75 per cent NaF, 5 to 7 per cent AlF_3 , up to 20 per cent Al_2O_3 and certain amounts of Al_4C_3 and metallic sodium.

The selective absorption of sodium fluoride by the carbon lining, high during the first months as the pores are filled, gradually slows down and ceases completely after a few months of operation.

124. The Efficiency of the Electrolytic Process

The electrolysis of molten cryolite-alumina baths obeys Faraday's Law exactly as the electrolysis of any other materials does. Hence,

$$\text{Gram equivalent of Al} = \frac{27}{3} = 9$$

In other words, it takes 26.8 A-h of electricity to produce 9 grams of aluminium from a cryolite-alumina bath. In practice, allowance has to be made for the current taken up by the re-oxidation of some aluminium and other side reactions. Therefore, it is customary to evaluate the efficiency of the bath in terms of cathode ampere-hour efficiency, K_{A-h} :

$$K_{A-h} = \frac{\text{Theoretical ampere-hour efficiency}}{\text{Actual current ampere-hour efficiency}} = \frac{It_{th}}{It_{ac}},$$

whence

$$It_{ac} = \frac{It_{th}}{K_{A-h}} = \frac{26.8 \times 10^6}{9 \times K_{A-h}} \text{ per ton of Al} \quad (1)$$

The second important index is energy consumption:

$$W = \frac{VIt}{10^3} \text{ kWh/ton,}$$

where

I = current, amperes;

V = voltage across the cell, volts;

t = time necessary for production of one ton of Al;

10^3 = proportionality factor.

Substituting It_{ac} from Eq. (1), we obtain:

$$W = \frac{V \times 2.98 \times 10^3}{K_{A-h}} = \frac{2980 V}{K_{A-h}} \text{ kWh/ton}$$

In most cases the voltage across the cell is 4.3 to 4.5 volts. This voltage is the sum of the following quantities:

$$V_c = V_d + D\varrho l + I\Sigma R$$

where

V_d = decomposition voltage of Al_2O_3 (which is the sum of decomposition voltage proper and overvoltage and averages 1.7 volts under industrial conditions);

$D\varrho l$ = voltage drop across the bath depending on its resistivity (ϱ), current density (D) and electrode spacing (l); under industrial conditions it is 1.5 to 1.7 volts;

$I\Sigma R$ = voltage drop across conductors, electrodes and connections, varying from cell to cell between 1.0 and 1.6 volts.

The current efficiency is to a great extent dependent on the condition of the cell and at modern plants varies between 0.8 and 0.92. From this figure it is easy to find energy consumption per ton of aluminium:

$$W = \frac{2980V_c}{K_{A-h}} = \frac{2980 \times 4.5}{0.85} = 15,600 \text{ kWh/ton}$$

The actual energy consumption is somewhat greater due to voltage losses in the circuits supplying current to cell, in converters, during start-ups and anode effects. Therefore, about 17,000 kWh of energy is practically spent to produce one ton of aluminium.

In industrial practice, use is made of a reciprocal quantity: the amount of aluminium produced per kWh of energy, often called the energy efficiency, K_e :

$$K_e = \frac{1 \times 1000 \times 1000}{17,500} = 57.2 \text{ grams}$$

Modern aluminium-reduction cells produce 57 to 62 grams of aluminium per kilowatt-hour.

Both the current efficiency and the energy efficiency have a direct bearing on the economics of the process. In turn, they depend on the temperature and composition of the bath, electrode spacing, and current density.

Bath temperature. As has been noted elsewhere, an increase in temperature considerably raises the solubility of aluminium in the electrolyte and, consequently, its losses through secondary reactions.

Fig. 197 relates the current efficiency to bath temperature. At 940°C , the current efficiency is about 94 per cent and drops as the temperature increases. A decrease in temperature, however, will not improve the current efficiency infinitely. Below a certain limit varying with the bath composition, a solid phase will appear in the residue, the working of the cell will be upset and the current efficiency reduced.

Bath composition. This factor plays a very important part. Present-day practice uses baths with a cryolite ratio less than 3, i.e., with an excess of AlF_3 . A shift towards the greater sodium fluoride content reduces the current efficiency which is apparently due to an increase in the concentration of sodium ions and the deposition

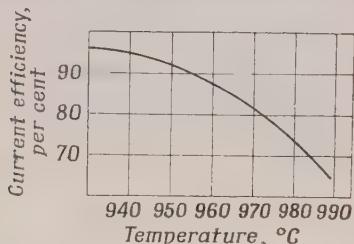


Fig. 197. Current efficiency vs. temperature

of sodium on the cathode—a factor which entails the waste of current (Fig. 198). Being of low solubility in aluminium, the sodium floats to the surface and burns.

Some producers work with a cryolite ratio of 2.2. The resulting excess of aluminium fluoride reduces the probability of sodium ions

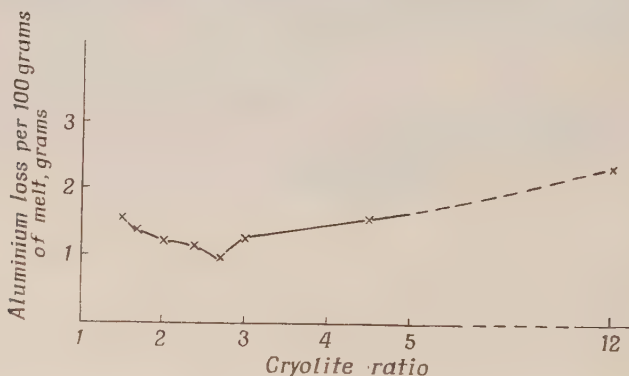


Fig. 198. Aluminium loss in molten cryolite with changes in bath composition (after Lozhkin)

discharging at the cathode and brings down the melting point of the electrolyte but raises its volatility.

Further reduction in bath temperature may be attained by adding to it small quantities of MgF_2 or CaF_2 . These additions also reduce the solubility of aluminium in the electrolyte and improve the current efficiency, if added in not too great amounts.

Electrode spacing. The diagram in Fig. 199 shows the current efficiency plotted against electrode spacing in an aluminium-reduction

cell after Abramov. As can be seen, the current efficiency rises with increasing electrode spacing. The explanation comes from the fact that with a greater distance from anode to cathode the aluminium dissolved in the bath has little chance to reach the anodes and to be oxidised there.

Current density. Referring to Fig. 200, the current efficiency sharply drops with decreasing current density, since the quantity of metal obtained by electrolysis is directly proportional to the current density while aluminium losses due to dissolution and oxidation are almost independent of it. Too high current density and too great

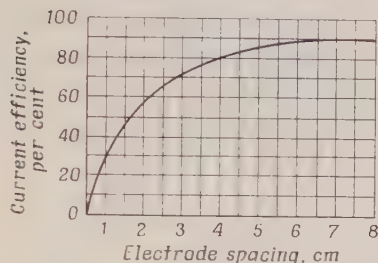


Fig. 199. Current efficiency related to electrode spacing

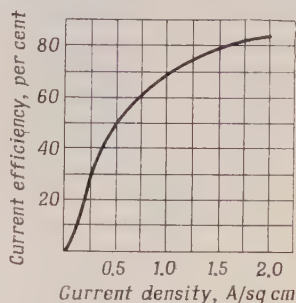


Fig. 200. Current efficiency related to current density (electrode spacing $l = 5$ cm; $t = 1000^\circ\text{C}$)

electrode spacing are not warranted, for this increases the voltage across the cell and, consequently, energy consumption per unit weight of aluminium.

The selection of optimum current density and electrode spacing is a difficult problem whose solution depends on prevailing conditions. In most cases, the cathode-to-anode distance is 4 to 6 cm, and it does not pay to increase it any further, because the gain in current efficiency will be cancelled by the increase in the cell voltage. Current density is ordinarily 0.7 to 1.2 A/sq cm.

Cell maintenance. This factor encompasses the maintenance of cryolite ratio, electrode spacing, and bath temperature. Good maintenance goes a long way towards eliminating undue anode effects, short circuits, current leakages and voltage losses across the contacts.

125. Improvements in Reduction Cell Design

Many important changes have been made in the design of the aluminium-reduction cell since the advent of commercial aluminium production.

Prior to 1940 aluminium manufacturers mainly used pressed and baked carbon anodes. Although still in use at some plants, they are giving way to continuous self-baking anodes which offer the following advantages:

- (a) elimination of anode pressing and baking;
- (b) elimination of stub ends inevitable in the case of pressed and baked anodes;
- (c) the possibility to build bigger reduction cells;
- (d) ease of fume withdrawal;
- (e) ease of maintenance.

A cell using a continuous anode is shown in Figs. 201 and 202.

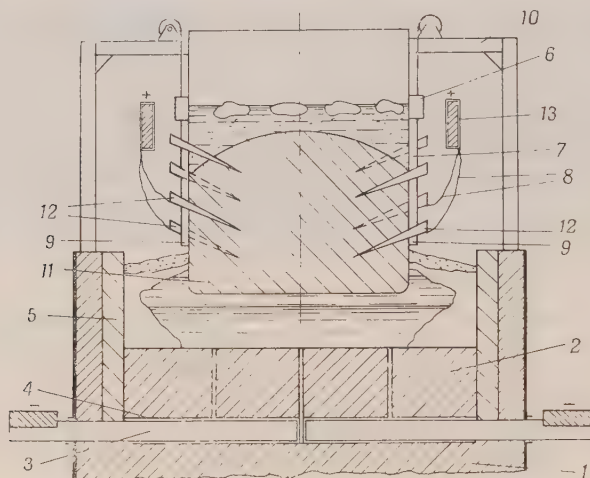


Fig. 201. Diagrammatic drawing of a cell with a continuous self-baking electrode and side-mounted rods

The shell of the cell is set in brickwork supported by a concrete foundation in which are embedded the anchor bolts of the shell. On the inside the shell is lined with two or three courses of firebrick 1 overlaid with a heavier lining of rammed carbon enclosing pressed and baked carbon blocks 2 serving as cathodes.

Current is supplied to the cathodes by substantial steel rods 3. Contact between the rods and carbon blocks is provided by cast iron 4 filling the space between the rod and blocks. Usually, one steel rod is embedded in one or two carbon blocks. The joints between the blocks are rammed with carbon. The side walls of the chamber are lined with carbon slabs 5 electrically insulated from the shell.

The self-baking continuous anode 11 works as follows: the anode carbon material is charged into a rectangular aluminium jacket.

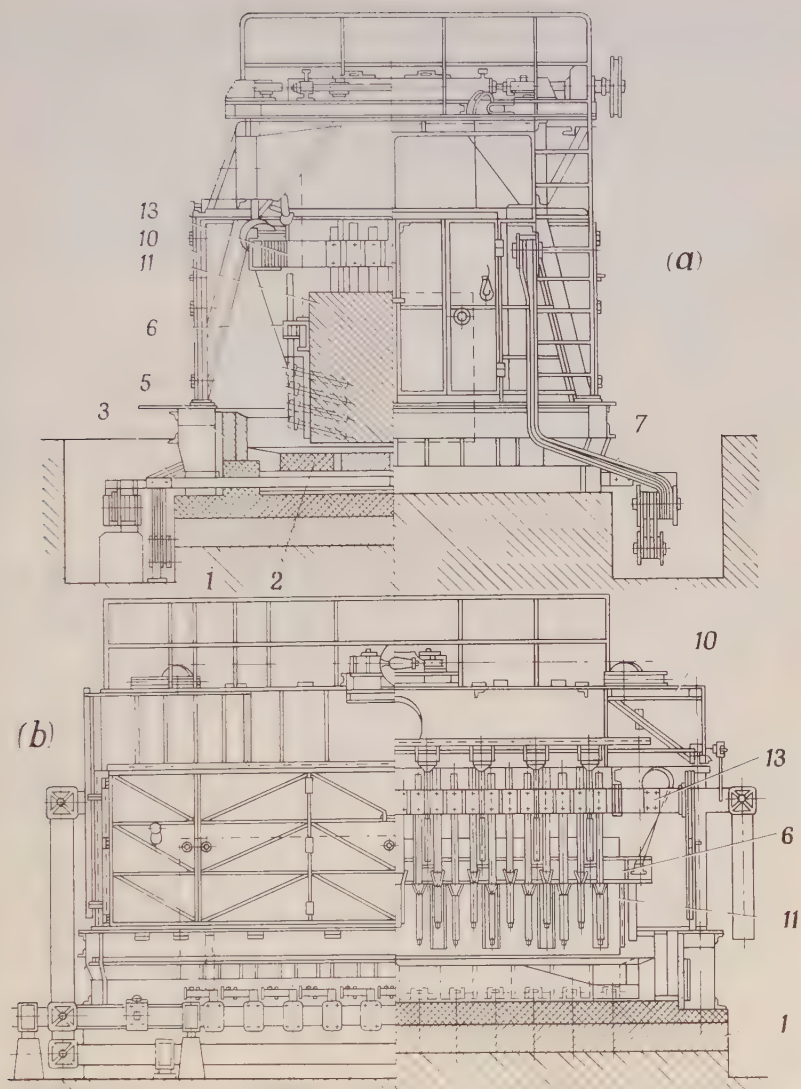


Fig. 202. Continuous-anode cell:
(a) end elevation; (b) side elevation

At the top of the jacket the carbon material is in a pasty condition: as it descends in the jacket it is baked into a dense block by the heat of the bath. The pressure of the pasty material on the jacket walls (1 or 2 mm thick) is counteracted by a strong frame 6 which envelopes the shell at the top. Welded to the frame are vertical stiffeners 7. The frame also serves as a support for the anode.

Current to the anode is conducted by steel rods 12 driven into the anode body. The rods are usually arranged in four rows, with 16 to 25 rods in each row. The two lowermost rows of rods are connected by flexible conductors 8 which are taken to the main aluminium busbar 13.

The anode is suspended over the bath so that it is free to move up and down—an important requirement for normal operation of the cell. Here is one of the possible suspension arrangements.

The rods in the lowermost row bear upon shackles 9 made fast to the shell stiffeners and so attached to the anode frame 6. Fastened to the corners of the frame are four link rods which are connected to the lifting mechanisms mounted on a stationary frame 10. This same frame also carries curtains to shut off the fumes evolved from the bath.

In recent years there has been a trend towards anodes to which current is supplied from above. Fig. 203 gives a schematic representation of such a cell. Its cathode is essentially the same as in the cell just discussed. Current to the anode is conducted by two, three or four rows of vertical steel rods 1. These rods also hold the anode above the cell. The rods are located at different distances above the bottom of the anode. As the anode wears away, the respective rods are in turn pulled out and driven in at a new position. The holes left are filled with liquid carbon material. After some time, the rod fuses with the baked anode.

Cells with top current connections offer the following advantages:

- (a) the superstructure of the cell is simplified;
- (b) the evolution of gases is reduced, and so the gases are better withdrawn and purified;
- (c) the servicing of the anode and other operations are easier to do.

Cells with top current connections may operate at up to 150,000 A; as a corollary, less energy is required per unit weight of aluminium and labour productivity is raised.

All types of cells operate on direct current supplied by mercury-arc rectifiers (or other converters) located nearby.

Most efficiently mercury-arc rectifiers operate at 600 to 800 volts. The average voltage, V_{av} , required for one cell with allowance for losses across buses, conductors and connections and also for the voltage rise due to the anode effect is about 5 volts.

Therefore, 120 to 160 cells are connected in a series. The number

of cells which may be connected to a given d.c. source is given by the formula:

$$n = \frac{V_{source}}{V_{av}}$$

A series of cells is usually located in one or two buildings. Small cells are normally arranged in four rows, while bigger cells in two rows in the building.

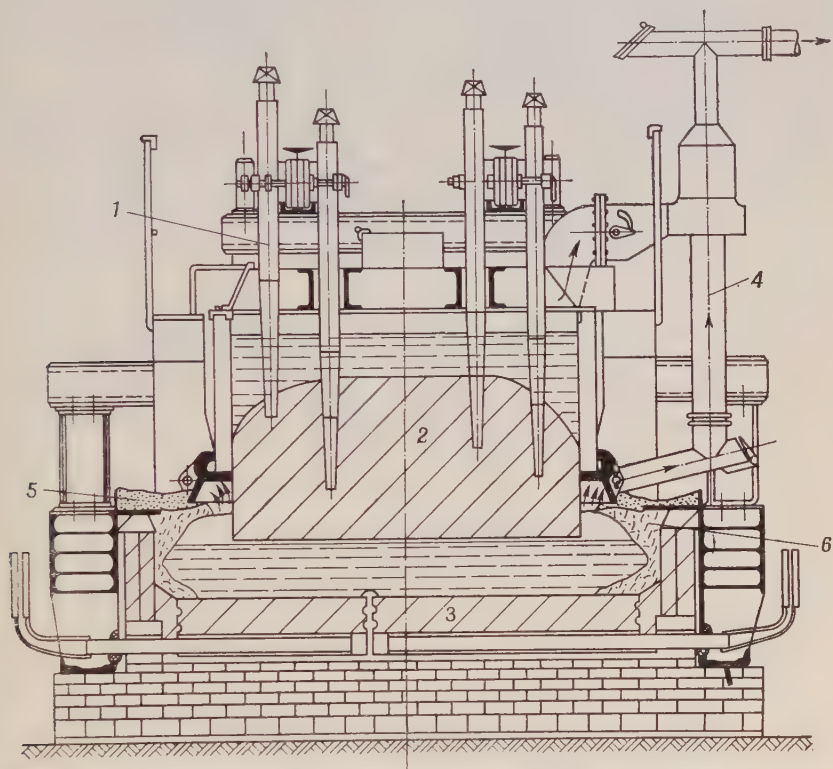


Fig. 203. Diagrammatic drawing of a continuous-anode aluminium-reduction cell with top-mounted current connections:

1—current-conducting rods; 2—anode; 3—cathode carbon block; 4—gas-withdrawal system; 5—alumina layer; 6—crust

The building should have ample ventilation and reliable electrical insulation of the floor, bus ducts and other parts.

Servicing the Cell. Different points are to be watched in starting up, running or shutting down a cell. Starting-up and shutting-down take very little time, since a cell can normally operate for 2 to 4

years. Our discussion will, therefore, be devoted to the care of a cell using a continuous anode during the normal course of operation.

Most of the time the cell requires no attendance, and one worker is quite able to take care of several cells during a shift.

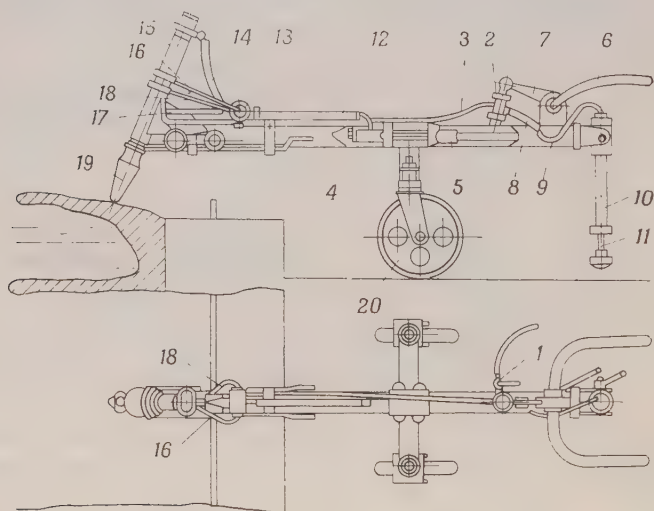


Fig. 204. Air-operated crust-breaker developed by Snezhko:

1—air valve; 2—plunger switch; 3, 8, 9, 12, 14, 16, 17, 18—hoses; 4—auxiliary cylinder; 5—auxiliary piston; 6—handle; 7—lever; 10—lifting cylinder; 11—rod; 13—air distributor; 15—striker cylinder; 19—point tool; 20—two-wheel trolley

The care of a cell with a continuous anode may be divided into the following steps:

- (a) addition of a fresh charge of alumina to the bath;
- (b) care of the electrolyte;
- (c) adjustment of electrode spacing and bath temperature;
- (d) withdrawal of aluminium from the cell;
- (e) care of the anodes.

Addition of a fresh charge of alumina. When the alumina content of the bath drops to about 0.5 per cent, an anode effect takes place, thus indicating that a fresh charge of alumina must be added to the bath. To do so (Fig. 204), the attendant breaks the crust with an air-operated rabble, pushes the alumina down, stirs it in, and charges more alumina on top.

If allowed to persist for a long time, the anode effect may upset the working of the cell, mainly by overheating the bath. To prevent this from happening, the procedure should be as follows: the crust is broken on an area of about 2 metres, the alumina spread on this

area is pushed down and stirred in with a perforated skimmer, and a dry wooden pole or board is dipped in the bath. The boiling action around the pole speeds up the dissolution of the alumina and cuts short the anode effect. After the "flare-up" is stopped, the remaining crust is broken and more alumina is stirred in. With this method, the anode effect can be stopped inside 1 to 3 minutes.

It is good practice to allow an anode effect to occur once in three to five days. For this reason, a fresh charge of alumina has often to be added to the bath before a voltage rise occurs. Skilled operators can detect the imminent voltage rise by outward signs half an hour to an hour in advance and add more alumina to the bath at that moment. Work is in hand in the Soviet Union on the continuous charging of alumina into the bath—a very important prerequisite for automated care and adjustment of the cell.

Care of the electrolyte. The quality of the electrolyte has a direct bearing on both the efficiency of electrolysis (current and energy efficiencies) and the quality of the aluminium produced.

The composition of the bath changes continuously throughout cell operation. During the first months, the lining selectively absorbs sodium fluoride, while the impurities added to the bath with alumina decompose the cryolite. Furthermore, some electrolyte is lost by volatilisation. This calls for constant watch on the quantity and composition of the bath, which is done by taking electrolyte samples daily and determining the cryolite ratio from the appearance of the fracture or by means of proximity analysis. Lack in aluminium fluoride or sodium fluoride, if there is any, should be made up for by adding the respective salt to the alumina on the crust and by stirring it in with the next fresh charge of alumina.

The quantity of electrolyte in the cell is determined by inserting an iron rabble into the cell vertically for 30 to 40 sec. The appearance and colour of the crust solidifying on the rabble will give an indication about the metal level and the depth of the electrolyte. Normally, the electrolyte should be 15 to 25 cm deep. If its level drops below that point, more cryolite should be added by the same method as alumina, sodium fluoride or aluminium fluoride. If the level has dropped much, molten electrolyte should be taken from another cell.

Adjustment of electrode spacing and bath temperature. The distance between the underside of the anode and the metal surface, or electrode spacing, is all-important for normal operation of the cell, because the temperature of the bath rises as the spacing increases, and vice versa. The electrode spacing can be varied at will by raising or lowering the anode. A convenient check on the electrode spacing is provided by voltage readings. Yet, direct measurement of the distance should also be taken, for the voltage may be affected

by some other factors (the formation of aluminium carbide on the cell bottom, for example). The electrode spacing should be adjusted after the anode has been cleared of the cryolite crust (after an anode effect or a tapping).

Withdrawal of the aluminium from the cell. The metallic aluminium sinks and collects on the cathode bottom. According to the formulas given earlier, a cell operating on a current of 70,000 A will have a daily output of about 500 kg of aluminium. It is a good plan to withdraw the aluminium at large time intervals, since the withdrawal somewhat upsets the normal run of the cell. Usually, this is done every two or three days, using either a siphon or a vacuum ladle. In older installations, tap holes were used to run off the liquid aluminium, but experience has disproved this method.

A siphon (Fig. 205) is a cast-iron T-piece the side branch of which is dipped into the aluminium in the cell and the lower end into a receiver, while the top end is used to build up a suction in the siphon. The receiver must be placed below the metal level in the cell. If the siphon is not to be clogged by solidifying metal or cryolite, it is heated to 150-250°C prior to the withdrawal and is lowered into the cell by crane. Then a small ladle full of liquid aluminium is put into the receiver, and the lower end of the siphon is dipped into it. As soon as the requisite suction is built up in the siphon, the liquid metal begins flowing from the cell into the receiver. When the aluminium has filled the receiver to a depth of 200 to 300 mm, the ladle is taken away, and the lower end of the siphon is submerged into the metal in the receiver.

A vacuum ladle (Fig. 206) requires a higher vacuum, and so the equipment used is more complicated than in the case of siphon pouring. On the other hand, no cell-side pits are required and the construction of the electrolysing department is simplified.

As more aluminium is withdrawn from the cell, its level drops and the distance from the anode to the metal surface increases, as does the voltage across the cell. As a precaution against the waste of power and the overheating of the bath due to the increased electrode spacing, the anode should be gradually lowered, watching that the voltage across the cell does not deviate by more than 0.5 volt from normal. Nor should too much aluminium be withdrawn from the cell, since this inevitably upsets its thermal balance.

Care of the anodes. A suitable example is provided by a cell using a continuous anode and side current connections. According to its physical condition, a continuous anode may be divided into four zones (Fig. 207).

Zone I is a dense coked material; from above this zone is bounded by the isotherm 400°C. Sometimes this zone is referred to as the "baking cone", and a periodical check is kept on its size.

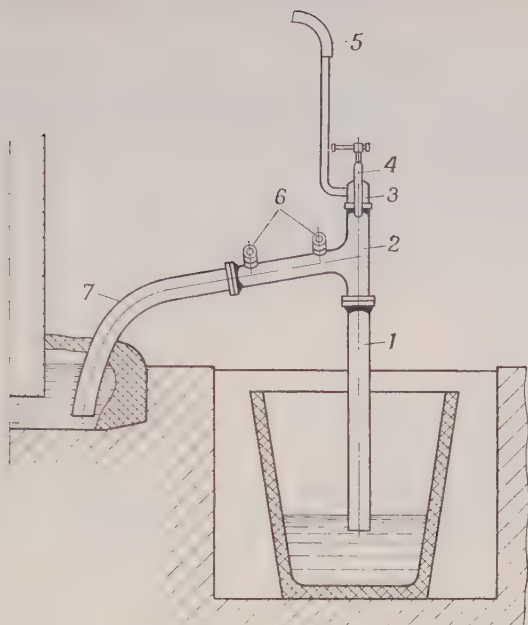


Fig. 205. Siphon for aluminium withdrawal from cells:
 1—pipe; 2—T-piece; 3—hood; 4—clamp; 5—hose; 6—lifting rings; 7—elbow

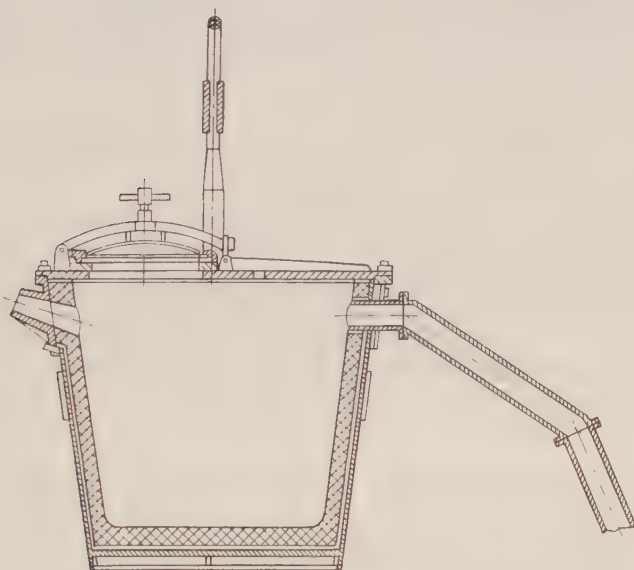


Fig. 206. Vacuum ladle for aluminium withdrawal from cells

Zone *II*, or the "coking zone", is located between the isotherms 400 and 360°C. It is in this zone that the coke skeleton is formed, and the pores formed are filled with liquid anode mass coming down from the top layers of the anode. As a result, a strong and dense anode is produced.

Zone *III* is situated between the isotherms 360-140°C. In this zone the material consists of solid carbon particles and liquid binder, the latter beginning to decompose and volatilise due to heat.

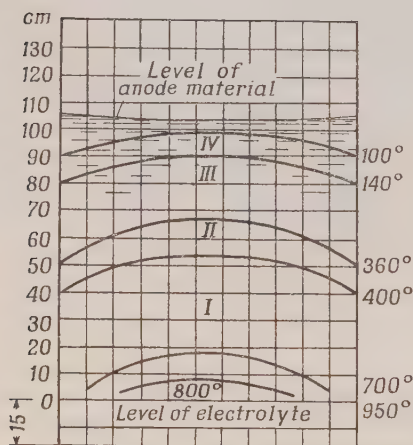


Fig. 207. Temperature gradients in a continuous anode

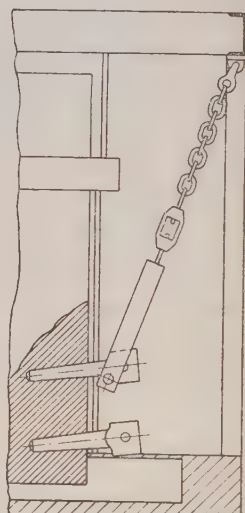


Fig. 208. Temporary braces for continuous anodes

In zone *IV*, or above the isotherm 140°C, the material softens.

As the electrolysis proceeds, the anode wears away due to oxidation, the electrode spacing is increased, and the anode frame has to be lowered together with the current-conducting rods and anode. When the distance between the lower row of rods and the molten electrolyte is reduced to about 10 cm, the flexible conductors (see Fig. 201) are reconnected from the lowermost row of rods to the third one, and then the rods in the lowermost row are withdrawn from the anode.

A very important point to watch is that the lowermost row of rods not only supply current to the anode but also hold it. So, before withdrawing the rods from the anode, it should be hung by the second-row rods from the supporting frame by means of temporary braces (Fig. 208).

The rods are withdrawn by an air-operated machine (Fig. 209). After that, the anode frame is raised until the suspension shackles of the frame are level with the current-conducting row of rods and the temporary braces become slack. Now the temporary braces may be removed, and the anode can again be raised or lowered by

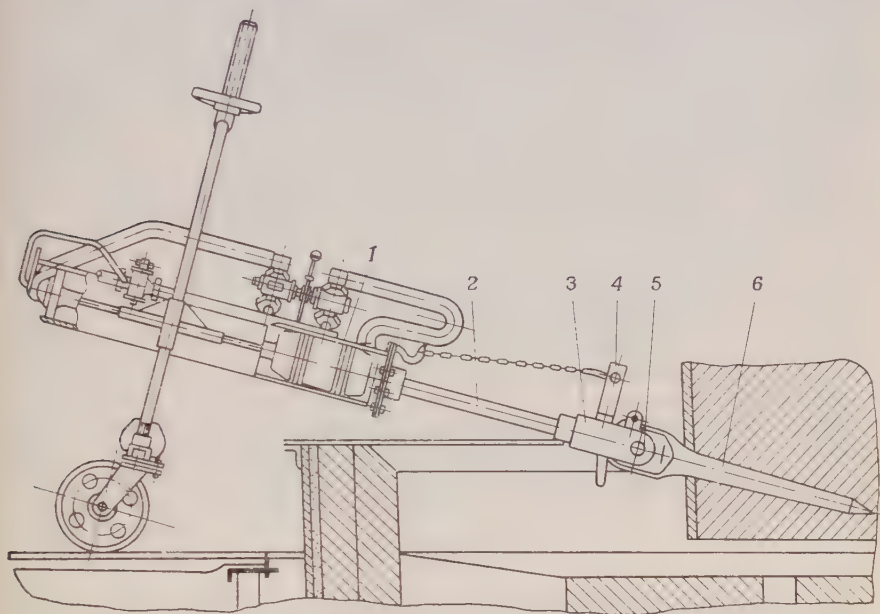


Fig. 209. Diagram showing the removal of a rod from a continuous anode by a Snezhko air-operated puller:

1—cylinder; 2—spindle; 3—grip; 4—tension wedge; 5—opening; 6—rod

means of its hoisting unit. The withdrawn rods are dressed and cleaned. After one day or two, a new (fourth) row of rods is driven into the anode.

That three rows of rods are driven into the anode while only one is used for current supply is because less force is necessary to drive a rod into the anode while it is soft at the top, without causing it to crack up.

As the anode wears away, an additional section is riveted to the top of the anode jacket, and the anode mass is poured into it from a steel bottom-discharge box handled by an overhead crane.

The aluminium anode jacket is built up about every month, and a fresh charge of anode mass is added every seven to ten days.

For a good bond between the fresh charge of anode material and the working anode, the surface of the latter should be thoroughly cleaned of dust. The jacket is filled with the anode material so that its top is 1 to 1.1 metres above electrolyte level and the layer of semiliquid material in the anode core is at least 25 cm deep.

Cells using vertical rods supplying current from above require fewer man-hours for anode maintenance. The basic operation in this case is to reposition the rods as the anode wears away. This is done when the end of a rod is within 25 cm of the anode underside. Rods are withdrawn by a suitable puller which first gives a rod a turn and then pulls it out of the anode. A quarter to a third of all the rods are repositioned at a time, because the rods should be staggered at different levels. The rest of maintenance operations (charging, cleaning, etc.) are the same as for anodes with side current connections.

All the materials (alumina, cryolite, anode mass, rods, etc.) and electrolysis products (aluminium, skimmings and the like) are handled within the shop by overhead cranes and electric trucks. In some cases, alumina is delivered to the cells by airslides and pneumatic conveyers. At all of the Soviet aluminium works the gaseous products of electrolysis are withdrawn from the cells and are either discharged into the atmosphere through stacks up to 120 metres high or treated for the recovery of gaseous fluorides and alumina dust.

126. Aluminium Refining

The crude aluminium withdrawn from the reduction cell contains metallic, non-metallic and gaseous impurities.

The impurities iron, silicon, sodium, potassium, titanium, copper, and magnesium may find their way into the metal either from the raw materials or due to careless servicing.

The non-metallic impurities alumina, electrolyte, aluminium carbide, coal particles, etc., may come either from the bath or from the receiver during and after the metal is run off.

Hydrogen enters the metal either during electrolysis or from the lining of the receiver and other pouring equipment.

All of these impurities affect the mechanical and casting properties, electrical conductivity and corrosion resistance of the metal.

According to the relevant U.S.S.R. State Standard, primary aluminium, which is the product of the cell after remelting, is marketed in nine grades (Table 48). The lowest five grades can be obtained by remelting and chlorination, while the top four grades require a more sophisticated treatment.

Refining by chlorination is carried out in ladles. A chlorination unit is shown in Fig. 210. The aluminium-filled ladle is placed

Table 48

Classification and Analysis of Primary Aluminium in Ingots

Grade designation	Analysis, per cent					
	Min. aluminium	Max. impurities				
		Fe	Si	Fe + Si	Cu	total impurities
AB0000	99.996	0.0015	0.0015	—	0.001	0.004
AB000	99.99	0.0080	0.0025	—	0.005	0.01
AB00	99.97	0.015	0.015	—	0.005	0.03
AB0	99.93	0.04	0.04	—	0.01	0.07
A00	99.7	0.16	0.16	0.26	0.01	0.30
A0	99.6	0.25	0.20	0.36	0.01	0.40
A1	99.5	0.30	0.30	0.45	0.015	0.50
A2	99.0	0.50	0.50	0.90	0.02	1.0
A3	98.0	1.1	1.0	1.80	0.05	2.0

under a hood. The hood has an opening through which a pipe is led in to admit the chlorine gas from a cylinder. It takes 10 to 15 minutes to treat one ton of aluminium with concurrent stirring.

Safety rules require that chlorine cylinders be placed in a separate room outside the main building, for the gas may injure attending personnel. The gases evolved during the treatment are withdrawn from beneath the hood by a ventilation unit. The treatment is carried out at a temperature of 720 to 750°C. Admitted by a graphite or quartz pipe fitted with a bubbler, chlorine is uniformly distributed throughout the volume of metal in the ladle and vigorously reacts with some of the aluminium to form AlCl_3 . Vapours of the aluminium chloride (boiling at 180°C) cause the non-metallic impurities suspended in the metal to float to the surface. In addition to the non-metallic impurities, the hydrogen dissolved in the aluminium and some metallic impurities succumb to the treatment. Chlorination affects the metals whose chlorides have a greater free energy of formation at the temperature of the process than has aluminium chloride.

Referring to Fig. 241, only calcium, sodium (potassium) and magnesium are capable of forming chlorides in the presence of much aluminium at 700 to 1000°C. The chlorides thus formed float to the surface as a grey loose powder which is removed by a perforated skimmer.

After chlorination, the aluminium that is to be cast into pigs is remelted in resistor-type reverberatory furnaces (Fig. 242).

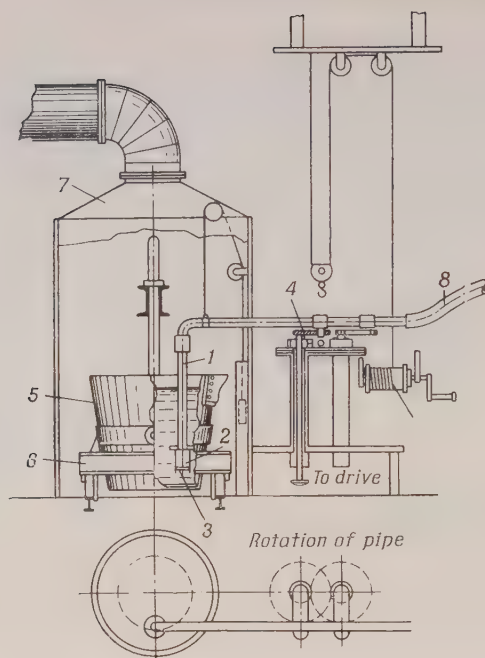


Fig. 240. Plant for aluminium chlorination in ladles:

1—chlorine inlet; 2—bubbler; 3—chlorine outlets (eight to ten holes 12 to 15 mm in dia); 4—platform and rotation mechanism; 5—ladle; 6—bogie; 7—chlorination chamber; 8—rubber hose

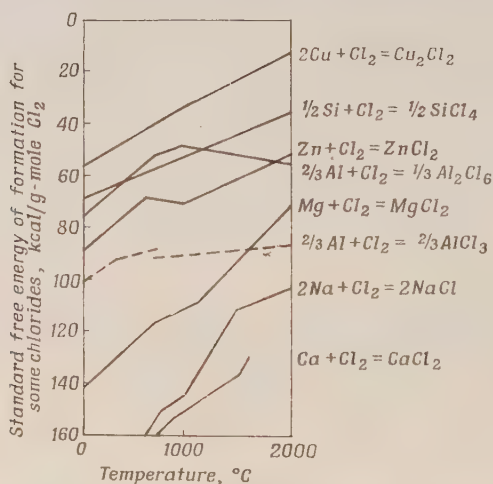


Fig. 241. Changes in the free energy of formation for some chlorides related to temperature

This type of furnace has a metal shell which is the shape of a half-cylinder at the bottom and is set up with its trunnions on four pyramid pedestals. In the inside the furnace is divided into two fore-chambers and a collecting chamber. The lining is of firebrick. The resistors wound with Ni-Cr wire are mounted in the roof of the furnace, and the tap hole is located in one of the long walls. The molten metal is run off by tilting the furnace by means of a jack positioned at the middle portion of the shell.

The remelting treatment serves a twofold purpose: (a) the metal is further refined of non-metallic impurities and gases as it is allowed to settle at the requisite temperature for a long time; and (b)

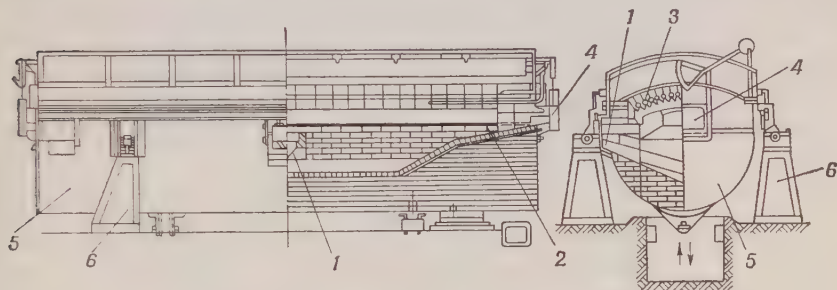


Fig. 212. Electric resistor furnace:

1—tap hole; 2—fore-chamber; 3—Ni-Cr resistors; 4—charging door for ingots; 5—shell; 6—columns

irregularities of composition of the different cell-withdrawals are equalised, giving a large amount of metal of one grade.

Electrolytic refining produces high-purity aluminium. Several methods have been developed to date. Commercially, use is made of the three-layer (Hoopes) process investigated in detail by Guskov et al. Electrolytic refining is carried out in a cell in which there are three horizontal layers; the lowest layer is a liquid aluminium-copper alloy anode; above this is a layer of electrolyte consisting of anhydrous fluorides and chlorides; and floating on top is the cathode of pure liquid aluminium. At the operating temperature the specific gravity of the electrolyte must be greater than that of the aluminium but lower than that of the alloy anode.

The electrolyte usually has the following composition: BaCl_2 , 60 per cent; AlF_3 , 23 per cent; and NaF , 17 per cent. This mixture has a specific gravity of 2.7 at the operating temperature (while that of aluminium under the same conditions is 2.3).

If the anode is not to float to the surface, it should contain at least 25 per cent copper in which case the anode alloy will have a specific gravity of 3.0 to 3.5.

The Hoopes process has much in common with the electrolytic refining of copper, the only difference being that instead of an aqueous solution and solid electrodes use is made of a molten electrolyte and liquid electrodes. Current is carried over by the ions of

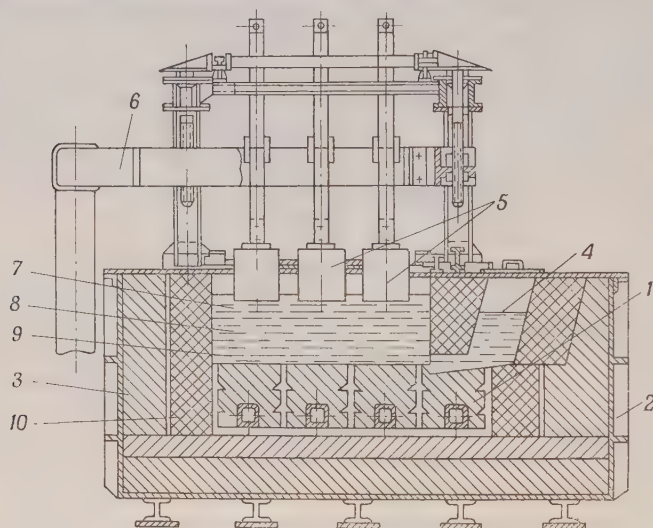
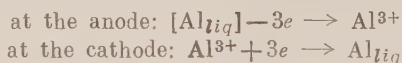


Fig. 213. Three-layer aluminium electrolytic cell:

1—cathode blocks; 2—shell; 3—side lining; 4—charging pocket; 5—cathodes; 6—cathode busbar; 7—refined aluminium; 8—electrolyte; 9—anode alloy; 10—magnesite lining

aluminium which appear at the anode and travel towards the cathode where they deposit as metallic aluminium. The entire process may be presented as follows:



The more electropositive impurities cannot pass from the anode into the electrolyte as long as the anode contains enough aluminium. The more electronegative impurities do pass from the anode into the electrolyte but cannot deposit at the cathode as long as the concentration of aluminium ions in the electrolyte and even at the cathode is high, because their deposition potential is higher than that of aluminium.

Fig. 213 shows a cell for three-layer electrolysis. Crude aluminium is periodically added to the anode through a special pocket, and the pure aluminium collecting at the cathode is ladled out.

As the electrolysis proceeds, the anode layer and electrolyte gradually become enriched in the impurities. If the cathode alu-

minium is not to be contaminated, both the anode alloy and electrolyte should be changed at regular intervals.

The electrolysis is carried out at 760 to 800°C. The anode layer is kept about 200 to 250 mm deep, and the electrolyte 150 to 120 mm deep. It is well advised to keep the aluminium layer on the cathode at least 10 cm thick and spray it with a thin coating of powdered electrolyte as a precaution against oxidation. The voltage across the cell is maintained at 6 to 7 volts. The purity of the refined metal is as high as 99.999 per cent. This process is, however, very expensive and is employed on a limited scale.

Many attempts have been made to develop other refining processes, including those based on the recovery of aluminium with low-melting metals (zinc, magnesium and mercury). A brief outline of the magnesium process, as most acceptable, follows.

The magnesium process serves to refine secondary aluminium, mainly duralumin. The latter is melted with 25 to 30 per cent Mg. This type of alloys have a melting point of about 500°C where the solubility of iron is sharply reduced and it appears in the residue as crystals of AlFe_3 . Part of the silicon forms light-weight magnesium silicides which float to the surface. At the same time some iron combines with the manganese. Then the aluminium-magnesium alloy is separated from the crystals of intermetallic compounds of iron, silicon and manganese by filtering the melt through basalt grit in a vacuum at a temperature of 510 to 520°C. The iron content of the filtrate does not usually exceed a few hundredths of one per cent.

The filtered aluminium-magnesium alloy is heated in a vacuum induction furnace (Fig. 214) fitted with a condenser, to drive off the magnesium. The zinc, if there is any in the alloy, will also be distilled off by this treatment.

The distillation of the magnesium and zinc is carried out at 900 to 950°C and a residual pressure of 0.1 mm Hg. The condenser should be maintained at about 200°C. Given these conditions, the magnesium and zinc will vaporise from the metal being refined and settle on the walls of the condenser as clusters of crystals. For a charge of 3 tons the operation occupies seven hours. After the magnesium has been driven off, hydrogen is admitted into the furnace under a gauge pressure of 20 mm Hg. By this time, the condenser walls will have been heated by the Ni-Cr resistors to 750°C. The magnesium and zinc are melted and run off through tap holes. The remaining aluminium is poured out by tilting the furnace.

The aluminium thus refined usually has the following composition: Fe, 0.1 per cent; Mg, 0.2 per cent; Si, 0.5 per cent; Zn, 0.05 per cent. It takes 2000 to 2300 kWh of electricity and 100 to 120 cu m of hydrogen to refine one ton of metal.

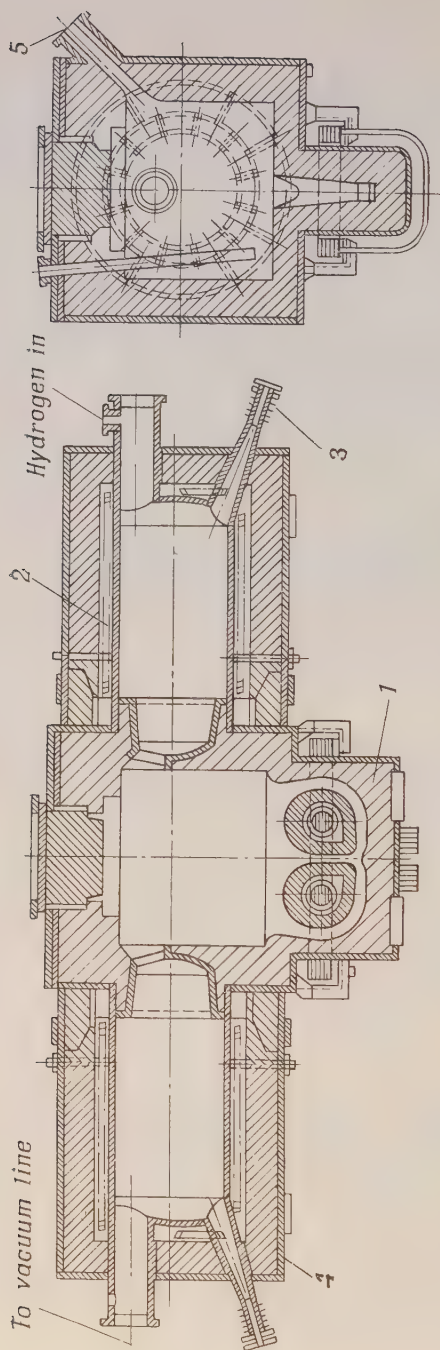
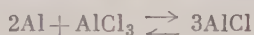


Fig. 214. Vacuum induction furnace for distilling off magnesium and zinc from aluminum alloys:
 1—furnace; 2—retort heaters; 3—tap hole for Mg-Zn alloy; 4—retort; 5—aluminum tap hole

Of late, much research has been done on the refining of aluminium by the *subcompound method*. As will be recalled, the outer shell of the aluminium atom has three electrons two of which are balanced and move in the 3s subshell, while the remaining electron which is in the 3p subshell is unbalanced and is more loosely attached to the nucleus than are the 3s electrons. In losing the 3p electron, aluminium becomes a univalent ion producing compounds of the lowest valency of the type AlCl, AlF, etc. These compounds will be formed if aluminium is heated to 1000°C or more and aluminium chloride (or fluoride) is passed over it. The respective gaseous subcompounds will form according to the reactions:



On cooling down to 700 or 800°C, these compounds break up into aluminium and aluminium chloride (fluoride). The impurities contained in the source aluminium are left behind. This method produces aluminium of up to 99.9995 per cent purity.

Aluminium of extra-high purity may also be obtained by *zone recrystallisation*. This process consists in the following: an aluminium rod 350 mm long and 15 to 20 mm dia is placed in a thoroughly washed and fired boat made from very pure graphite. The boat is then placed in a quartz tube along which a narrow induction heater is moved, capable of melting the rod within a zone 20 to 25 mm long. Moving the induction heater ten or fifteen times from end to end along the rod at the rate of 1 mm/min will produce a 200 to 250 mm rod of extremely pure aluminium from the original rod.

127. Auxiliary Operations in the Production of Electrolytic Aluminium

After refining, aluminium is cast either into pigs or wire bars for subsequent rolling. Pigs are cast in casting machines in which an endless chain of moulds supported by trunnions moves past a pouring ladle or a resistor furnace (Fig. 215). Wire bars in the Soviet Union are generally cast by a semicontinuous method (Fig. 216)

A semicontinuous casting unit consists of two shafts and mould stools carrying from four to ten water-jacketed moulds 2. The hydraulically operated mould stools 12 move down as the increasing weight of the pig or ingot causes the piston attached to the stool to squeeze oil out of the cylinder (omitted in the illustration). The travel of the mould stools is 2.8 m. The shafts are used in turn: while an ingot is solidifying in one of them, the other is being prepared for casting (the moulds are lubricated, the stool raised, the tundish set up, etc).

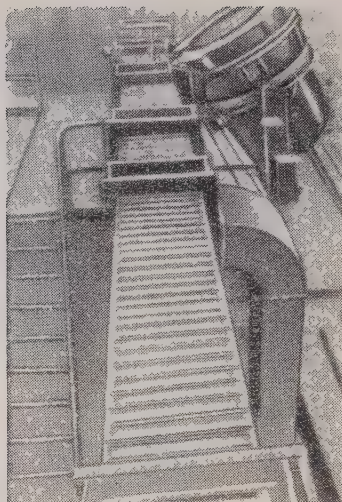


Fig. 215. Aluminium pig casting machine

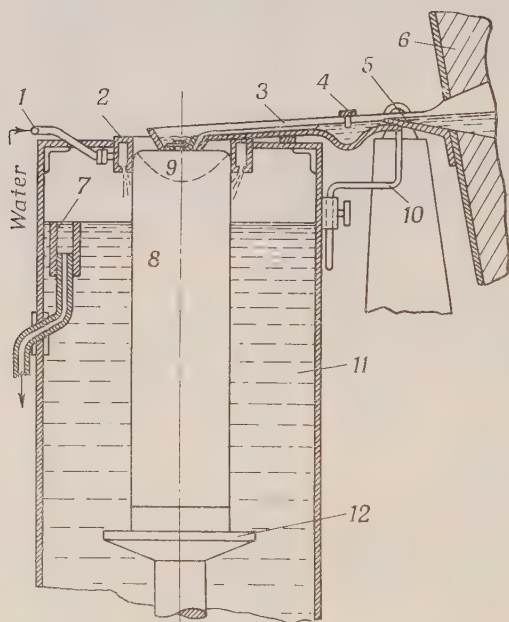


Fig. 216. Diagram of semicontinuous aluminium pig casting:

1—pipe carrying water to mould; 2—mould; 3—launder; 4—slag trap; 5—tap hole; 6—teeming furnace; 7—water out; 8—solidified metal; 9—molten metal; 10—launder support; 11—water; 12—hydraulically operated stool

128. Economics of Aluminium Production

As has been noted elsewhere, electric power constitutes a sizeable item on the balance-sheet of aluminium production. A breakdown of production costs is given in Table 49.

Table 49

Approximate Production Costs of One Ton
of Primary Aluminium

Item	Share in total costs, per cent
<i>Materials (direct and indirect)</i>	
Alumina	31.8
Fresh cryolite	1.9
Aluminium fluoride	3.4
Anode mass	13.5
Sheet aluminium	0.4
	Total 51.0
<i>Power</i>	
Process	28.4
Drive	0.6
	Total 29.0
Wages	8.0
Depreciation	6.0
Departmental expenses	3.0
Departmental cost	97.0
Factory overhead	3.0
Factory cost	100.0

Referring to the table, the cost of the materials (both direct and indirect) constitutes the largest single item, with alumina accounting for about a third of all expenses. Putting it another way, the cost of aluminium may above all be reduced by cutting down the expenses on alumina. Theoretically, it takes 1.89 tons of alumina to produce one ton of aluminium. Actually, more alumina is required, since some of it is lost as dust. By properly handling the dust problem, it is possible to reduce the cost of aluminium by 0.5 to 0.6 per cent. Still greater reduction in the cost of aluminium may be effected through the recovery of alumina from the mud, by cutting down losses of sodium aluminate solution and hydroxide of aluminium

in handling and of alumina in calcination. A further saving may be achieved by utilising more of the exhaust steam (from evaporators) and the heat of the flue gases. Steam recovery is especially important in the case of the Bayer process where much steam is consumed in the autoclave.

The consumption of fluorides may be cut down by recuperating the cell gases and recovering their fluorine content.

The anode gases contain up to 40 mg/cu m of fluorine, about 100 mg/cu m of pitch, and 90 mg/cu m of dust (AlF_3 , Al_2O_3 , and Na_3AlF_6). These gases can be treated with a weak solution of sodium carbonate in tower scrubbers in order to recover their values and to render them harmless before they are discharged into the atmosphere. Unfortunately, not all manufacturers do so, allowing these gases to be discharged untreated (which is against the law) through stacks 100 to 120 metres high. Where recovered, the values can be returned to the process, thereby halving the consumption of fluorides, and hence the cost of aluminium may be further reduced by 3 to 5 per cent.

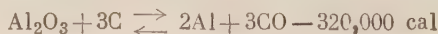
Another line of attack in cutting down the cost of aluminium is to use cheaper sources of electricity, economical semiconductor converters (such as silicon and germanium rectifiers), and more economical cells. The latter goal may be attained by building cells with low voltage loss around the entire circuit and by using more conductive electrolytes than cryolite. Incidentally, a good proportion of the current passing through the cryolite bath is converted to heat which is wasted.

The proper maintenance of the cell (which includes electrode spacing, electric contacts, anode effects, bath temperature and composition, replacement of bolted joints with welded where possible, etc.) may also go a long way towards bringing down power consumption per unit weight of aluminium and, consequently, production costs.

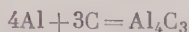
Finally, process mechanisation and automation may help greatly in reducing the production costs of aluminium. A change-over at some plants to continuous leaching and digestion has made them still more adaptable to automation with the result that the consumption of steam and electricity has been reduced, labour productivity raised, and production costs brought down.

129. Thermal Processes of Aluminium-alloy Production

Thermal Processes Defined. The reduction of aluminium by carbon may be presented as follows:



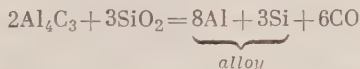
The lowest temperature for this reaction to take place is about 2000°C, which is very close to the boiling point of aluminium. It is easily attainable in arc furnaces. Unfortunately, the aluminium thus reduced vaporises and reacts with carbon to form aluminium carbide:



At this temperature the pressure of aluminium carbide vapours is very high and they mix with aluminium vapours. As the temperature decreases, the equilibrium of the first reaction is shifted to the left, and an appreciable amount of aluminium oxide appears in the products of the reaction. The condensation of the vapours produced by the reduction of pure alumina with carbon gives a condensate consisting of a mixture of aluminium, aluminium carbide and alumina not suitable for any use.

As an alternative, alumina may be reduced in the presence of an element having a higher boiling point than has aluminium and dissolving it in a liquid state. The product will be an alloy of aluminium and the element used. The solvent may be either silicon with a boiling point of 2600°C or iron which boils at 3000°C. At a given temperature, the partial pressure of aluminium vapours over an alloy is much lower than above pure aluminium, and less aluminium will be lost. The formation of aluminium carbide will be prevented by the aluminium dissolving in the other metal.

Investigations have shown that silicon is a more attractive proposition for this purpose, since cheap silica instead of elemental silicon may be used. In addition to alumina, this process also reduces silica. The latter has a lower temperature of reduction and a high dissociation pressure, and so an appreciable amount of silicon appears before aluminium vapours are produced. Silicon does not practically dissolve aluminium carbide. Furthermore, aluminium carbide enters in the following reaction with silica at elevated temperatures:



Thus direct reduction of Al_2O_3 and SiO_2 can give silicon-aluminium alloys containing up to 70 per cent Al.

Silicon-aluminium Alloys. In the case of electrothermal processes, silicon-aluminium alloys may be obtained not only from pure alumina and silica, but also from kaolins, low-iron but high-silica bauxites, cyanites, etc.

The quality of the source materials varies with the intended application of a given alloy, the main criterion being its iron oxide

content. The latter may be high if the alloy is to deoxidise steel, or it must be as low as possible if the alloy goes to make silumin in which the iron content should not exceed 0.35 per cent.

The reducing agents can be materials of low ash content, such as charcoal, peat and oil coke, and anthracite.

Silico-aluminium is melted in arc furnaces with a current-conducting carbon hearth. The furnace is so run that accretions form on its walls to protect the firebrick, magnesite brick and carbon blocks. The charge is in sintered or otherwise agglomerated form. The arc voltage is 55 to 70 volts.

The furnace top is closed to prevent escape of the furnace gases. Normally, a solid crust of partly fused charge is formed in the furnace above the reaction zone. This crust handicaps the normal descent of the charge material and may sometimes give rise to a considerable expulsion of the charge, should the gas pressure increase too much. As a precaution, the crust must be periodically broken up and the charge forced down.

Before running off the high-aluminium alloy, lumps of quartz are added to the molten metal in order to destroy the aluminium carbide. As a rule, the silico-aluminium is tapped twice a shift. The tap is burned through with an electric arc. Moulds for silico-aluminium are lined with carbon blocks or rammed with moulding sand. This process produces aluminium-silicon alloys with the following composition: Al, 25 to 70 per cent; Si, 28 to 70 per cent; and Fe, 1 to 1.5 per cent.

It takes 12,000 to 16,000 kWh of energy, 1.3 tons of reducing agent (charcoal) and 0.24 ton of carbon electrodes to make one ton of such alloys.

Electrothermal Silumin. Electric-furnace aluminium alloys run from 28 to 70 per cent Si. Being too brittle, they are unsuitable for engineering purposes and are only used as steel deoxidisers. On the other hand, aluminium alloys containing 13 per cent and less silicon, known as silumins, are alloys of importance to engineering because of their excellent casting qualities, including fluidity and freedom from red shortness, and high resistance to corrosion. Silumins may be obtained by melting pure aluminium and electrothermal silico-aluminium or by removing excess silicon from the latter. The mechanism of the process can be easily understood from the two-component fusibility diagram of the system Al-Si (Fig. 217).

When cooled to below 1040° , molten 50-per cent alloy throws out crystals of silicon, and the composition of the remaining liquid phase follows the liquidus. By the time the alloy cools to 580°C the composition of the liquid phase will have approached an eutectic. If, at this temperature, the liquid phase is separated from the

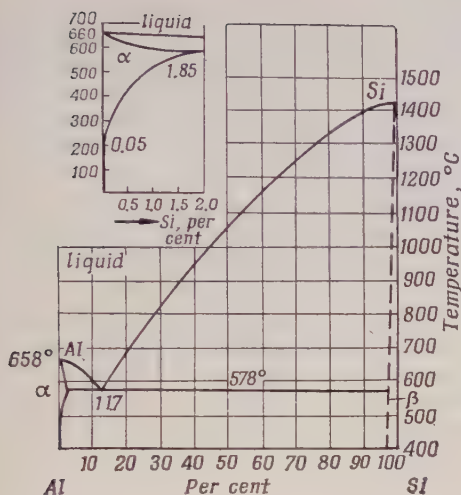


Fig. 217. Constitution diagram of the system Al-Si

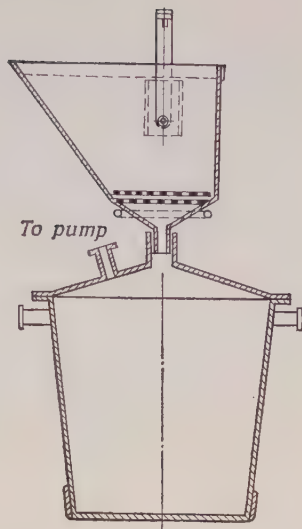


Fig. 218. Filter for molten silico-aluminium

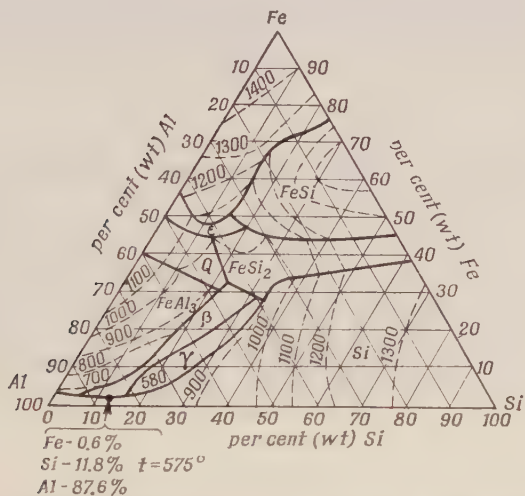


Fig. 219. Three-component fusibility diagram of the system Al-Si-Fe

solid phase, the products will be excess silicon and the eutectic silumin we are after. The silicon crystals are filtered out, as has been described, by passing the mixture through a 6-mm bed of crushed basalt or coarse sand placed between perforated steel plates. A pressure is usually built up above the filter, or a vacuum beneath it, in order to speed up and bring the separation to completion. Fig. 218 shows an apparatus for vacuum separation.

High-quality silumin may be obtained by this method if the source alloy contains very little iron. Otherwise, more than 0.6 per cent iron will enter the filtrate. Why this is so can be easily understood from the three-component fusibility diagram of the system Al-Si-Fe in Fig. 219. The arrow in the diagram points to the ternary eutectic with a melting point of 575°C, usually filtering after the partial crystallisation of high-iron silico-aluminium.

Thus, the high-iron aluminium-silicon alloy produced electrothermally may be separated into electrothermal silumin containing 12 per cent Si and 0.6-4.0 per cent Fe and the filter residue carrying up to 80 per cent Si which may be successfully utilised for the thermal reduction of magnesium, as steel deoxidiser, and for other purposes.

The properties of silumin are appreciably impaired with increasing iron content. Currently, work is under way on methods for the removal of iron from electrothermal silumin.

The detrimental effect of iron on silumin may be partially offset by adding to it small amounts of manganese or chromium. The current commercial practice, however, is to produce electrothermal silumin from ores containing no iron oxides.

130. Recovery of Other Values from Aluminium Ores

In addition to aluminium, aluminium ores sometimes contain considerable amounts of silicon, iron, titanium, potassium, sodium, calcium and also minute quantities of zirconium, chromium, phosphorus, gallium, vanadium and some other elements. Not all of them can be recovered, however, with existing methods.

By far the best recovery of other values is in the case of apatite-nepheline ores which serve as the source of fertilisers, alumina, sodium carbonate, potash, cement, etc., with a very negligible proportion of the material going to the dump.

With the Bayer and Deville-Pechiney processes, too much red mud still goes to waste, although its utilisation may prove profitable.

In recent years, much headway has been made in the recovery of other values from aluminium ores in connection with the production of vanadium oxides and metallic gallium at aluminium works.

Gallium was discovered by de Boisbaudran by a spectroscopic method in 1875. Four years before him, Mendeleev had predicted the existence of gallium as eka-aluminium. Gallium is a metallic-grey metal which melts at 30°C to a silvery liquid. It boils at 2230°C , and is used in high-temperature thermometers with scales graduated for up to 1300°C . It is nearly as hard as lead and has a specific gravity of 5.9 when solid and 6.09 when liquid.

Although gallium is widely distributed in nature, its minerals of commercial value are unknown. It mainly occurs in minute concentrations as an associate of aluminium and zinc in ores and in many coals. The tar residues of gas works sometimes contain up to 0.75 per cent gallium.

Gallium is a much stronger poison than are mercury and arsenic. When exposed to dry air at ordinary temperatures, gallium remains unattacked; when heated, it combines with oxygen to form the white oxide, Ga_2O_3 . Under certain conditions, other oxides (GaO and Ga_2O) may also be formed. Gallium hydroxide, $\text{Ga}(\text{OH})_3$, is amphoteric and is therefore easily soluble in both acids and alkalis, forming with them gallates similar in properties to aluminates. For this reason, gallium accompanies aluminium at all the stages of aluminium production. An increased concentration of gallium is present in the anode alloy of the electrolytic aluminium refining, residues of the Bayer alumina liquors, and the liquors after the incomplete carbonation of sodium-aluminate solutions.

Accordingly, gallium may be recovered from these by-products without upsetting the production flow at aluminium works.

The Bayer alumina liquors may be treated for the recovery of gallium by two-stage carbonation. During the first stage, carbonation is slow, and about 90 per cent of the aluminium hydroxide is precipitated. The precipitate is separated by filtration, and the filtrate is CO_2 -treated again to precipitate the gallium and remaining aluminium as hydroxides. The residue thus obtained may contain up to 1.0 per cent Ga_2O_3 .

Much of the aluminium may be precipitated from the sodium aluminate liquor as fluorides. To this end, hydrofluoric acid is added to the gallium-bearing sodium-aluminate liquor. When pH is below 2.5, a good proportion of the aluminium is thrown down from the liquor as aluminium fluoride and cryolite (Na_3AlF_6). The gallium and some aluminium remain in the solution. When the acid solution is neutralised with sodium carbonate to pH 6.5, the gallium and aluminium appear as a residue.

The further separation of the aluminium from the gallium may be accomplished by treating the aluminium-gallium hydroxides with milk of lime carrying some sodium hydroxide. The gallium passes into solution, and the bulk of the aluminium remains in the

residue. The gallium is then precipitated with carbon dioxide; the resulting residue carries up to 25 per cent Ga_2O_3 .

There exist other methods for the recovery of gallium oxide from sodium-aluminate liquors.

The anode alloy left over from the electrolytic refining of aluminium by the three-layer method may contain 0.1 to 0.3 per cent gallium. The latter can be recovered by treating the anode alloy with a hot alkaline solution. The aluminium and gallium pass into solution, while the copper and iron are retained in the residue.

Pure gallium compounds are produced by dissolving gallium chloride in ether.

Chapter XVIII

THE METALLURGY OF MAGNESIUM

131. Magnesium and Its Alloys—a General Outline

Magnesium is a silvery white metal. With a specific gravity of 1.738 (at 20°C), it is the lightest structural metal. It is in Group II of the Periodic Table and has the atomic configuration 2-8-2 for which reason it is divalent in all of its compounds. Of interest is the high pressure of magnesium vapours (see Table 50).

Table 50

Pressure of Saturated Magnesium Vapours as a Function of Temperature

Temperature, °C	Vapour pressure, mm Hg	Temperature, °C	Vapour pressure, mm Hg
227	1.26×10^{-7}	727	7.78
527	0.1	827	36.40
627	1.62	927	127.0
650	approx. 2.5	1107	760.0

When magnesium is exposed to dry air, a film of oxide forms on its surface, protecting it from further oxidation—the factor responsible for the high corrosion resistance of pure magnesium in which respect it exceeds structural iron.

Distilled water does not practically attack magnesium. In damp air, its corrosion, however, is aggravated. Magnesium resists the attack of hydrofluoric and chromic acids and alkaline solutions. This is also true of kerosene, petrol and mineral oils. It is, however, liable to the attack of aqueous salt solutions (except for fluorides) and is soluble in many mineral and organic acids. The corrosion resistance of magnesium decreases with increasing content of impurities.

Solid magnesium (in pigs or substantial articles) will not burn till heated above its melting point (654°C), if not isolated from atmospheric oxygen. When covered with a blanket of flux, magnesium may be safely heated and melted. As thin ribbons or in finely divided form, however, it will burn, evolving intense heat—a prop-

erty utilised in photographic flashlights. Magnesium is non-magnetic and non-sparking on impact or in friction.

Magnesium is mainly used in alloy form. Its mechanical properties and workability are improved by additions of aluminium and zinc; an addition of manganese improves its corrosion resistance. The compositions of the most commonly used magnesium alloys are summarised in Table 51.

Table 51

Composition of Magnesium Alloys

Alloy	Composition, per cent				Total impurities, max. per cent
	Al	Zn	Mn	Mg	
MЛ4	5-7	2-3	0.15-0.5	Remainder	0.60
MЛ5	7.5-9.3	0.2-0.8	0.15-0.5		0.60
MЛ6	9.0-11.0	max. 2.0	0.10-0.5		0.60
MГC1	—	—	1.8-2.5		0.20
MГC2	3.0-4.0	0.3-0.7	0.20-0.50		0.19
MГC5	7.5-8.7	0.3-0.7	0.20-0.50		0.20

Magnesium alloys can be cast by sand, permanent and die-casting methods into intricate shapes, and also welded and machined. Because of these properties coupled with low specific gravity magnesium is widely used in the manufacture of aircraft and automobile engines. Modern planes may have as many as 400 parts in magnesium alloys, totalling between them over one ton in weight.

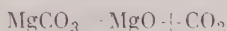
Magnesium has won recognition as an addition to cast iron improving its mechanical properties and as a reducing agent in the manufacture of titanium and other metals hard to reduce. The property of magnesium to evolve intense light and heat in burning are used in flares, tracer and incendiary shells and bombs.

132. Sources of Magnesium

Magnesium is never found native. Some important magnesium minerals used in magnesium manufacture are magnesite, dolomite, carnallite and bischofite.

Magnesite, or magnesium carbonate, answers the formula MgCO_3 . Usually it contains the impurities CaO , SiO_2 , Al_2O_3 and Fe_2O_3 . Only pure magnesite is suitable for magnesium production. The Soviet Union, with a number of major deposits, leads the world in magnesite output. Magnesium manufacture ranks third in magne-

site consumption after refractories and building materials. It uses caustic magnesite, or magnesium oxide obtained by the reaction



by calcining natural magnesite to 700-900°C.

Dolomite, or a double carbonate of calcium and magnesium, has the formula $\text{CaCO}_3 \cdot \text{MgCO}_3$. The usual impurities are quartz, calcite, and gypsum. The content and colour of the impurities determine the colour of the rock. Dolomite is widely distributed in nature and accounts for about 0.1 per cent of the earth's crust.

To be good for magnesium production, dolomite should have a $\text{CaO} \cdot \text{MgO}$ ratio of not over 1.54, the content of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2$ not over 2.5 per cent, and the content of alkaline metals not over 0.3 per cent. As is the case with magnesite, dolomite is calcined to a mixture of MgO and CaO before it is used for magnesium manufacture.

Carnallite, which is a natural chloride of magnesium and potassium, has the formula $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$. It usually has a pink, or yellow or grey tint, depending on the impurities present, and is extremely hygroscopic.

Carnallite is concentrated and treated hydrochemically to recover the bromine and some sodium and potassium chloride. The product left after this extraction is anhydrous sodium magnesium chloride, or artificial carnallite, which goes to make magnesium. An approximate composition of natural and artificial carnallite is given in Table 52.

Table 52

Per Cent Analysis of Carnallite

Carnallite	KCl	MgCl ₂	NaCl	H ₂ O	Insoluble residue
Natural	19.3	24.0	24.4	29.9	2.4
Artificial	24.4	32.2	4.2	38.8	0.1

Bischofite, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, is left after the treatment of natural carnallite. Inexhaustible reserves of bischofite are also contained in sea water which carries an average of 3.8 grams of MgCl_2 , 1.7 grams of MgSO_4 and 0.1 gram of MgBr_2 in one litre of water. A practical process has been developed and used for its extraction for several years. More often, however, magnesium chloride is extracted from salt lakes. To this end, the magnesium-bearing water is diverted into shallow ponds for solar evaporation and the precipitation of low-soluble sodium chloride, magnesium sulphate

and other magnesium-bearing minerals. The further evaporation of the brine produces bischofite. The product is delivered to magnesium works in steel drums or similar containers.

133. Production of Magnesium

In 1800, Sir Humphry Davy first made magnesium by the reduction of magnesium oxide with potassium vapour.

In 1833, Michael Faraday first electrolysed magnesium chloride to make magnesium.

In 1852, Robert Bunsen developed an electrolytic cell for the production of magnesium from fused anhydrous magnesium chloride. His cell used carbon electrodes and a porcelain diaphragm between the anodes and cathode. Thus, both Bunsen and Faraday may be credited with having founded the electrolytic process of magnesium production.

All the commercial processes for the production of magnesium may be classed into two broad systems: electrolytic and thermal.

Electrolytic processes consist of several stages of which the principal ones are the preparation of pure anhydrous magnesium salts, their electrolysis in the fused condition, and the refining of electrolytic magnesium. The individual processes differ in the source material used (which may be carnallite, magnesium chloride, etc.) and the method of its preparation (magnesite chlorination, dehydration of magnesium chloride, etc.).

Electrolysis of aqueous solutions of magnesium salts is technically unsound because magnesium is more electronegative than the hydrogen ions at the cathode and there is no method by which to reverse the condition.

Thermal processes are based on the reduction of magnesium oxide with either carbon, or silicon or any other reducing material at elevated temperature and a relatively high vacuum.

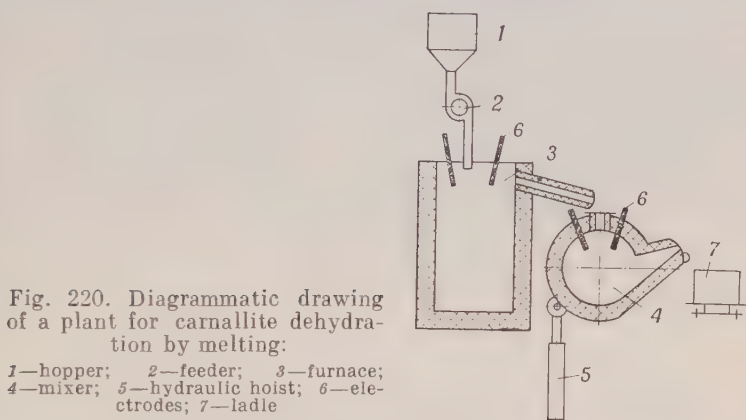
A thermal process consists of (1) the preparation of the reducing agent and source materials; (2) reduction, sublimation and condensation of magnesium vapour; and (3) smelting of the condensed crystals into pigs.

134. Preparation of Magnesium Chloride for Electrolysis

Dehydration of carnallite. Under normal conditions, carnallite forms crystals with six molecules of water ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$). When rapidly heated at atmospheric pressure to over 110°C or 120°C , it melts in crystallisation water. If heated slowly, however, nearly all crystallisation water may be driven off without melting because the melting point of hydrous crystals rises with decreasing water content.

The first stage of dehydration is usually carried out in rotary kilns 35 to 40 m long and 3 to 3.5 m in diameter. The treatment occupies

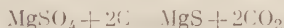
about two hours, with the temperature of the incoming gases not exceeding 550 to 600°C. The carnallite thus obtained carries 3 or 4 per cent water and some magnesium oxide (1 to 2 per cent). The second dehydration stage involves the melting of the carnallite in resistance furnaces in which heat is developed by the passage



of current from electrode to electrode through the carnallite charge. A resistance furnace is essentially a rectangular refractory-lined chamber with two steel electrodes passed through the roof and connected to the L.V. side of a single-phase transformer. The temperature in the furnace is maintained at 750 to 800°C. The molten carnallite is run off continuously down a chute into two mixers in turn. The mixers operate on the same principle as does the furnace (Fig. 220). In the mixers the molten charge is heated to 780-850°C and is allowed to settle, separating from the suspended magnesium oxide. Where the carnallite contains sulphates, crushed charcoal is added to the melt to remove as much as 90 per cent of the sulphur by the reactions



and

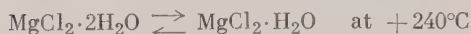


The molten and dehydrated carnallite carrying about 50 per cent MgCl_2 and 0.5 to 0.9 per cent MgO is run off and sent for electrolysis.

The dehydration of bischofite. Magnesium chloride forms hydrous crystals with 12, 8, 6, 4, 2 and 1 molecules of water.

Each of them is stable at a definite temperature and a change-over

from one hydrate to another occurs as follows:



When heated, crystals of hydrous magnesium chloride decompose at a relatively low temperature, and so rapid heating may result in melting and foaming. Furthermore, simple heating will not drive off all water from hydrous magnesium chloride as at over 200°C it hydrolyses to form hydrogen chloride.

In the temperature range $304\text{--}554^\circ\text{C}$ the following equation holds:



the equilibrium constant being

$$K = \frac{p_{\text{HCl}}}{p_{\text{H}_2\text{O}}}$$

Above 554°C the equilibrium may be expressed thus:



and the equilibrium constant will be

$$K = \frac{p_{\text{HCl}}^2}{p_{\text{H}_2\text{O}}}$$

From the two equations it follows that heating in air will not drive off all water without decomposing the magnesium chloride. To avoid decomposition of magnesium chloride, the equilibrium of the two last reactions should be shifted to the left. So, the ratio of the partial pressure of the HCl in the gaseous phase to that of water vapours must be greater than the equilibrium constants of these reactions at a given temperature, or

$$\frac{p_{\text{HCl}}}{p_{\text{H}_2\text{O}}} > K_1 \quad \text{and} \quad \frac{p_{\text{HCl}}^2}{p_{\text{H}_2\text{O}}} > K_2$$

This is the reason why bischofite is dehydrated in two stages. The first stage is carried out in a rotary kiln, with the bischofite slowly heated with a current of hot gases to obtain a product having 1.5 or 2 molecules of water in its crystals.

This operation must be closely watched because bischofite melts at 106°C . The formation of a liquid phase in the kiln slows down the

reaction appreciably, with the product depositing on the kiln walls to a point where its operation may be fully upset.

As more water is driven off, the melting point of the charge gradually rises, and the heating may be done with a counter-current of flue gases.

The second stage calls for heating at an increased partial pressure of the HCl in the gaseous phase. To meet this requirement, the heating is done in a current of HCl. Hydrochloric acid gas is either

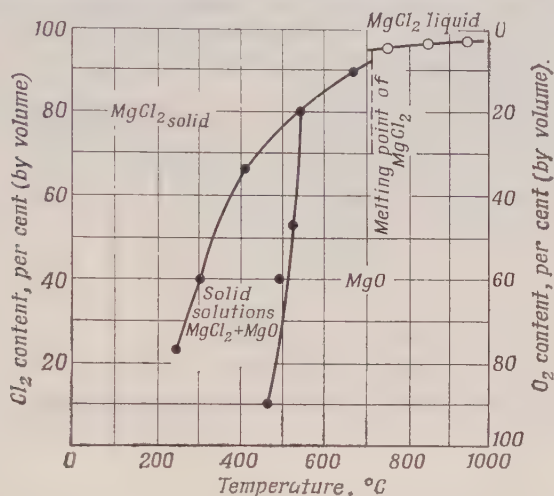


Fig. 221. Equilibrium diagram for the system $\text{MgO} + \text{Cl}_2 \rightleftharpoons \text{MgCl}_2 + \frac{1}{2} \text{O}_2$

●—●—● after Sukhodsky, Obukh and Kryagina;

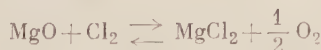
○—○—○ after Reznikov

introduced into the apparatus or, which is more convenient, produced in the kiln from the anode gases of the electrolytic cell and carbon according to the reaction:



The second stage may be carried out in both rotary kilns and in arc furnaces. In the latter case, the operation is conducted at a temperature above the melting point of anhydrous magnesium chloride, and the final product is molten magnesium chloride containing not more than 1.0 per cent MgO and 0.5 per cent H₂O.

Chlorination of magnesium oxide. Magnesium oxide may be chlorinated at elevated temperature with the chlorine gas according to the reaction

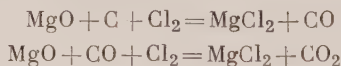


The equilibrium of this system has been investigated over a wide temperature range and is graphically shown in Fig. 221. Four fields stand out clearly in the diagram. The left-hand field identifies the solid MgCl_2 , the top right-hand field the molten MgCl_2 , the bottom right-hand field MgO and the middle field the solid solutions MgCl_2 and MgO .

Referring to the diagram, the formation of MgCl_2 is possible at a temperature of 250 to 300°C and a low concentration of chlorine (25 to 30 per cent by volume). The reaction, however, is slow. To be acceptable commercially, the treatment must be conducted at 500 to 700°C and a chlorine concentration of at least 80 to 90 per cent.

In practice, use is usually made of the anode gases from electrolytic cells which contain oxygen much in excess of the equilibrium concentrations for a gaseous phase at 1000°C. A way out is to fix the excess oxygen by carbon. The reducing material also serves to fix the oxygen produced by chlorination.

In the presence of a solid reducing material (coal or coke), the following reactions take place:



Investigations have established that chlorination is fairly complete at 800°C. Being exothermal, it requires very little extraneous heat.

The rate and completeness of chlorination is to a great extent dependent on the quality of the magnesium oxide and reducing material used. The research done at the U.S.S.R. Aluminium-Magnesium Institute has shown that both the reducing material and magnesium oxide must be pure, finely divided, intimately mixed and briquetted.

The success of the treatment also depends on the temperature at which the magnesite is calcined. If the temperature is too high, the resulting magnesium oxide will have a low reactivity. At one time, an attempt was made to improve the reactivity of magnesite by chlorinating briquettes of the so-called dry mix made up of raw (uncalcined) magnesite, oil coke and pitch as the binder. The attempt to combine calcination and chlorination proved unsuccessful, however, because much of the chlorine was wasted.

Some manufacturers apply chlorination to a solid mixture of magnesium oxide and a magnesium chloride solution. A vital drawback of this method is that the charge contains 10 to 12 per cent water and much chlorine is likewise wasted.

Magnesium oxide is treated in chlorinators (Fig. 222). A chlorinator is an electric shaft furnace which consists of a steel cylin-

drical shell lined with shaped refractory brick. Two rows of carbon electrodes are inserted at the bottom of the furnace, with three electrodes per row, spaced a third of the circle apart. The electrodes of one row are shifted through 60 degrees in plan with respect to those of the other row. The space between the rows of electrodes is filled with carbon resistor blocks capable of producing a temperature of up to 1000°C. The chlorine gas is introduced into the furnace through three inlets located between the two rows of electrodes. The molten

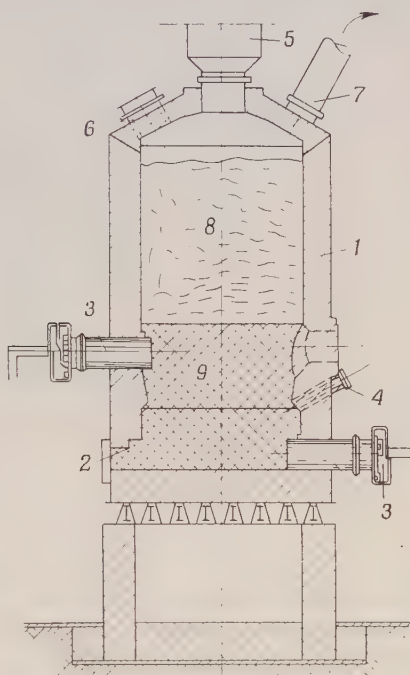


Fig. 222. Electric chlorinator:

1—refractory setting; 2—tap hole;
3—carbon electrode; 4—chlorine
inlet; 5—feed chamber; 6—man-
hole; 7—exhaust; 8—charge; 9—
carbon resistor blocks

magnesium chloride is run off through a tap hole at the bottom of the furnace. The materials are charged into the furnace at the top through a double bell-and-hopper feed chamber.

The burden in the furnace during chlorination may be arbitrarily divided into three zones. In the top zone 2 or 3 m deep the charge is heated by flue gases, and its water is driven off. At the bottom of this zone, the chlorine not used in the main reaction zone is absorbed.

The middle, or reaction, zone is responsible for chlorination proper which is accompanied by the fixation of the oxygen evolved. The temperature in this zone must be somewhat above the melting point of magnesium chloride (718°C); then the magnesium chloride

will melt, trickle down and expose the magnesium oxide not yet treated. A very vital requirement is that the charge must remain in lump form as far as the bottom of the reaction zone or else the chlorine gas will be unable to spread throughout the furnace uniformly.

The bottom zone filled with carbon resistor blocks generates heat and serves as a filter for the molten magnesium chloride. The particles of magnesium oxide entrained by the molten chloride are chlorinated in this zone by the rising current of chlorine. The temperature in this zone must be 150 to 200°C above the melting point of magnesium chloride so that it can flow freely through the packing onto the furnace bottom.

The magnesium chloride is run off every 3 or 4 hours into ladles with closely fitting lids. In these ladles it is taken to electrolysis cells.

The flue gases contain about 2.5 per cent HCl, about 20 per cent CO₂, and close on 25 per cent CO, the remainder being nitrogen and oxygen. The flue gases carry off with them about 100 g/cu m of vapours of magnesium, iron and silicon chlorides. The flue gases are poisonous and must not be discharged into the atmosphere. The usual practice is therefore to treat them for the recovery of their HCl content and to burn as a fuel (their calorific value is about 1000 kcal/cu m).

The choice of a method for the preparation of anhydrous magnesium chloride depends on the availability of raw materials. Other things being equal, preference should be given to chlorination, for it is simpler and cheaper than the dehydration of bischofite. A very vital consideration from this point of view is the supply of chlorine. The electrolysis of magnesium chloride results in magnesium and chlorine; of the total anode chlorine only 25 to 30 per cent is absorbed by the second stage of the dehydration of bischofite. Although the remainder (70 per cent) ought not to be discharged into the atmosphere, it is difficult to utilise, since it is strongly diluted with oxygen and nitrogen. If a plant runs only on magnesite, there will inevitably be a lack of chlorine, because some of it is lost in the process. A happy balance may be struck by proportioning magnesite and bischofite so as to make up for the loss of chlorine in the process. Furthermore, the second stage of dehydration may be advantageously combined with the chlorination of the magnesite.

Carnallite is less difficult to dehydrate than is bischofite. A straight carnallite bath is seldom used, however, because too much carnallite (10 tons per ton of magnesium) would be required and much electrolyte thrown away.

135. Electrolytic Production of Magnesium

After preparing anhydrous magnesium chloride, a suitable mixture of this salt with chlorides of potassium, sodium and calcium is electrolysed.

An electrolytic cell is shown schematically in Fig. 223. At 1 are graphite plates serving as anodes, and at 2 are steel plates used as cathodes.

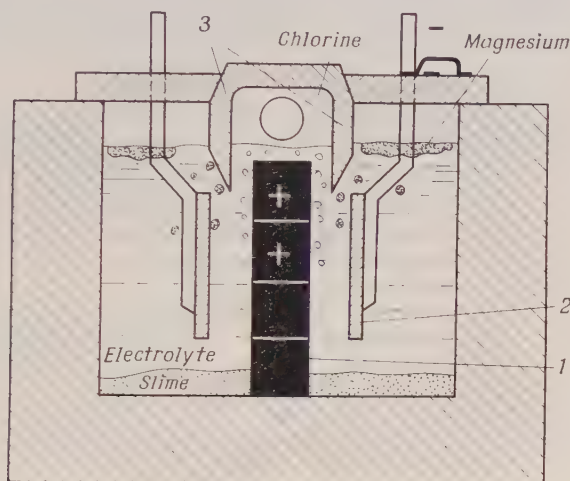


Fig. 223. Magnesium electrolytic cell

Under similar temperature conditions, the specific gravity of the molten electrolyte is greater than that of magnesium, and the latter produced at the cathode floats to the surface of the bath. The chlorine liberated anodically also floats to the surface. To prevent contact between the two products the cell is fitted with a hood 3, called the diaphragm, which also protects the cell from a short circuit by the molten magnesium.

In the process, anhydrous magnesium chloride is added to the bath from time to time to keep the bath within the required limits of composition. The magnesium which collects on the surface of the cathode space is periodically ladled out. The chlorine is swept out of the cell and recovered for, say, the chlorination of magnesium oxide.

Theoretically, it would be possible to use a bath of pure anhydrous magnesium chloride for the electrolytic production of magnesium. In practice, however, preference is given to a suitable mixture of several chlorides because pure magnesium chloride has

a very high melting point, low electrical conductivity and some other drawbacks. Carnallite is more attractive, since it usually contains some sodium chloride and has a lower melting point, a higher electrical conductivity, and dissolves magnesium not so eagerly. As a result, a carnallite bath is distinguished by a higher current efficiency and a lower power consumption.

Here is a brief outline of the essential properties of the electrolyte.

Fusibility. The ingredients of the bath have the following melting points: MgCl_2 , 718°C ; KCl , 768°C ; NaCl , 800°C ; and CaCl_2 , 774°C .

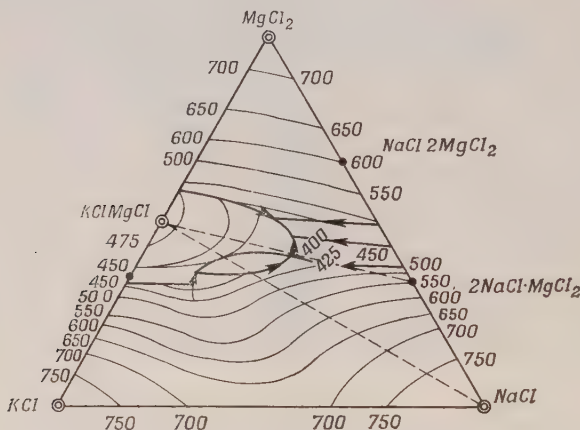


Fig. 224. Three-component fusibility diagram for the system KCl-NaCl-MgCl_2 (after Abramov)

Mixtures of these salts melt at a considerably lower point, as will be seen from reference to the three-component fusibility diagram of the system $\text{KCl-MgCl}_2\text{-NaCl}$ in Fig. 224. The actual composition of the bath may be varied within broad limits (see Fig. 225).

Specific gravity. The specific gravities of magnesium and carnallite are anywhere between 1.6 and 1.7 and are especially close to each other at 700°C —a temperature particularly good for electrolysis. The same applies to ternary electrolytes made up of MgCl_2 , KCl and NaCl . This feature is unfavourable for electrolysis, because the products of electrolysis may react with one another, thereby causing loss of energy. In order that the magnesium can rapidly float to the surface and separate from the rest of the bath, some “ballast” has to be added to the electrolyte. Use is ordinarily made of calcium chloride.

Electrical conductivity. The electrical conductivity of the bath depends on its composition. The least electrical conductivity is displayed by MgCl_2 , $1.17 \text{ ohm}^{-1}\text{-cm}^{-1}$ at 800°C , as against 2.02

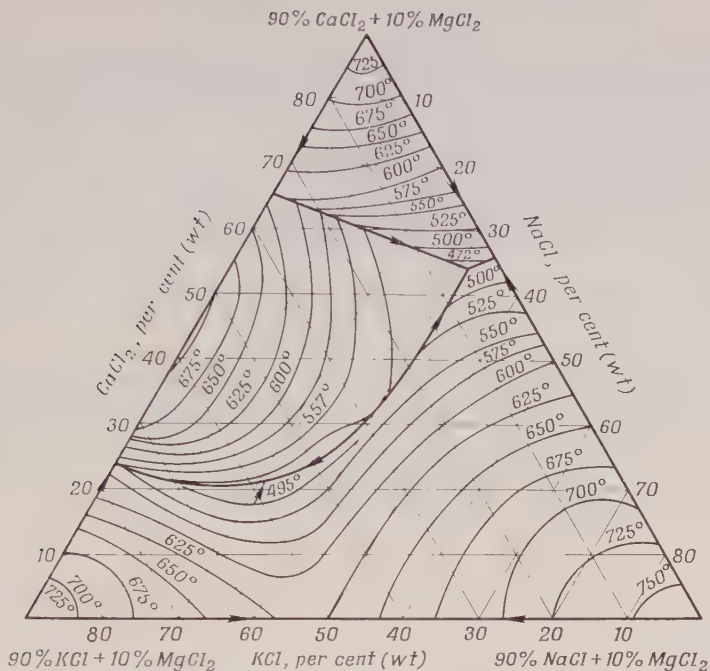


Fig. 225. Four-component fusibility diagram for the system KCl - NaCl - MgCl_2 - CaCl_2 with 10 per cent MgCl_2 (after Ivanov)

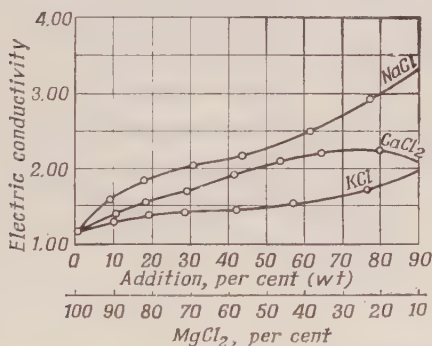


Fig. 226. Electric conductivity of MgCl_2 related to the content of other chlorides added to it (at 800°C)

for CaCl_2 , 2.42 for KCl and 3.57 for NaCl at the same temperature.

The diagram in Fig. 226 relates the electrical conductivity of magnesium chloride to the amount of alkali chlorides added to it. As follows from the chart, these additions considerably increase the electrical conductivity of the bath. It should be noted that the addition of several chlorides at a time changes the electrical conductivity of the electrolyte in a fairly complicated way (Table 53.)

Table 53

Electrical Conductivity of Composite Molten Baths
(after Batashov)

Molar per cent		Electrical conductivity, ohm ⁻¹ ·cm ⁻¹		Molar per cent		Electrical conductivity, ohm ⁻¹ ·cm ⁻¹		Molar per cent		Electrical conductivity, ohm ⁻¹ ·cm ⁻¹	
KCl + MgCl ₂	NaCl	at 700 deg. C	at 750 deg. C	KCl + NaCl	MgCl ₂	at 700 deg. C	at 750 deg. C	MgCl ₂ + NaCl	KCl	at 700 deg. C	at 750 deg. C
100	0	1.38	1.50	80	20	1.98	2.15	100	0	1.81	1.93
90	10	1.57	1.68	40	60	1.51	1.64	80	20	1.86	2.0
70	30	1.82	1.95	20	80	1.42	1.55	40	60	1.92	2.05
50	50	2.04	2.15	0	100	1.30	1.42	20	80	—	2.12
20	80	2.52	2.68								

Decomposition voltage. At the operating temperature of electrolysis all the ingredients of the bath (MgCl_2 , KCl , NaCl and CaCl_2) are ionised. At the anode only chlorine ions can discharge under such conditions, while at the cathode ions Mg^{2+} , Na^+ , K^+ and Ca^{2+} will be produced. Guskov et al. (U.S.S.R.) have carried out detailed studies into the possibility of sodium, potassium and calcium being produced at the cathode alongside with magnesium. It has been established that at the temperature of commercial electrolysis (750°C) the decomposition voltage of MgCl_2 is 2.6, of NaCl , 3.15, of KCl , 3.29, and of CaCl_2 , 3.24 volts. As the decomposition voltage of magnesium chloride is much lower than that of other chlorides, the predominant evolution of magnesium at the cathode in the case of equal concentrations (or, rather, equal activities of the cations) is unquestionable.

However, the commercial electrolyte can considerably vary both in temperature and the concentration of the various ions. In such a case, the reversible equilibrium potential of evolution, E , will be

$$E = E^\circ + \frac{RT}{nF} \ln C$$

where E is the electrode potential for an ion concentration C and temperature T , and E° is the potential for an ion concentration of 1 gram-ion per litre and a temperature of 298°K.

Consequently, should there occur any trouble in the operation of the cell, other metals, especially sodium, may well deposit on the cathode. This is the reason why the concentration of magnesium chloride in the bath should never be allowed to drop below 3 per cent.

Viscosity and surface tension. Pure molten magnesium chloride is three times as viscous as molten sodium and potassium chlorides. Its reduction has a favourable effect on the process. Apart from the viscosity of the bath, potassium and sodium chlorides also reduce the surface tension of magnesium chloride at the interface with the gaseous phase. Excessive surface tension is undesirable, for it hampers the coalescence of the metallic globules which collect at the surface of the cathode. Too low a surface tension is likewise undesirable, since the magnesium floating to the surface would break through the electrolyte film to be exposed to atmospheric oxygen.

The excessive decrease in the surface tension of the electrolyte due to the reduced MgCl_2 content is counteracted by CaCl_2 which, like all alkali-earth chlorides, increases the surface tension.

Solubility of magnesium in the electrolyte. Investigators disagree in their views on the mechanism by which magnesium dissolves in the electrolyte. Some believe that, when molten, magnesium forms both a true and a colloidal solution (so-called metallic fog). Others hold that a chemical interaction takes place between the magnesium and electrolyte which gives rise to subcompounds (i.e., compounds of lower valency). One way or the other, magnesium does dissolve in the electrolyte, entailing loss of energy due to the fact that the metal reaching the anode space is rechlorinated.

According to Zhurin, of all the ingredients of the electrolyte the highest solubility is displayed by molten magnesium chloride (0.3 per cent). An addition of alkali (sodium, potassium and calcium) chlorides reduces the solubility of magnesium.

Bath composition. Commercial practice shows that the quaternary electrolyte may have the following composition: MgCl_2 , 10 per cent; CaCl_2 , 45 per cent; NaCl , 30 per cent; and KCl , 15 per cent. If some carnallite is added to the bath, the CaCl_2 and NaCl content is reduced and that of KCl is raised to 70 or 75 per cent.

Some manufacturers improve the efficiency of the process by introducing other additives into the bath. Among them special mention should be made of NaF and CaF_2 . Their effect has been investigated in detail by Fedotyev and explained by Belayev and Zhemchuzhina. A wealth of experimental data shows that fluorides

increase the surface tension at the interface between the molten magnesium and the solid cathode; the globules of molten magnesium are held more strongly on the cathode surface and have more time to grow. NaF is more efficient than CaF_2 , because the former dissolves in the electrolyte more readily.

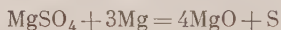
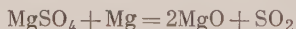
The impurities that may upset the process are above all moisture, sulphates, iron salts, and oxides of magnesium and boron.

According to Fedotyev and other Soviet investigators, every 0.1 per cent moisture in the electrolyte reduces the current efficiency by 1 per cent. The moisture is electrolysed with the production of hydrogen at the cathode. Some workers believe that the moisture reacts with the magnesium as follows:



As a result, some magnesium is lost not only chemically but also physically due to the fact that the magnesium oxide forming on the surface of magnesium globules hampers their coalescence and sometimes entrains them into the slime.

If present in the electrolyte, magnesium sulphate markedly impairs the current efficiency due to the reactions



accompanied by so-called gassing of the electrolyte.

Iron salts affect the electrolysis in that the deposition of magnesium on the cathode is retarded for a long time, even though the content of iron may be as low as about 0.1 per cent.

The effect of magnesium oxide on the electrolysis is other than electrochemical: it settles to the bottom of the cell as slime which entrains small globules of magnesium. The slime has to be discharged periodically, which is a very arduous job to do. Furthermore, some magnesium oxide settles on the cathode, and the magnesium is produced as finely divided globules which are slower to float than larger ones. Moreover, more magnesium is carried into the anode compartment to be rechlorinated. Boron oxide (B_2O_3) shows a similar though stronger effect.

In view of this, the salts that go to make a bath for electrolysis must meet stringent requirements as to their purity. The limits for impurities are as follows: H_2O , 0.1 per cent; SO_3 , 0.03 per cent; FeCl_3 , 0.04 per cent; MgO , 0.3 per cent; and B_2O_3 , not over 0.002 per cent.

Bath temperature. The melting point of a four-component electrolyte of an optimum composition is about 500°C and is not so critical as is the case with the electrolytical production of aluminium.

The lower limit of the process is 651°C, which is the melting point of magnesium. Electrolysis at 650 or 660°C produces solid pieces of magnesium which fail to float or coalesce efficiently.

As the temperature of the bath increases, the viscosity of the electrolyte is reduced, more magnesium dissolved in the electrolyte is carried by convection and diffusion into the anode compartment, and some chlorine is expelled into the cathode compartment to bring about an additional loss of metallic magnesium and energy. At the same time, oxidation becomes more pronounced, and so does the vaporisation of the magnesium floating on the surface of the bath due to an increase in its vapour pressure.

On the other hand, an increase in the bath temperature increases the electrical conductivity of the electrolyte and reduces the requisite voltage across the cell. In view of all these factors, the electrolysis is carried out in the temperature range 690-720°C.

Other variables of the process. It takes 26.8 A-h to produce 12.16 grams of magnesium (1 gram-equivalent). Hence, 1 A-h produces 0.454 gram of Mg, and the energy consumption in kWh per ton will be

$$W = \frac{V(It)_{theor}}{10^3} = \frac{V \times 26.8 \times 10^6}{10^3 \times 12.16 K_c} = 2210 \frac{V}{K_c}$$

The effect of the composition and temperature of the bath of the current efficiency (K_c) has already been discussed.

Other things being equal, an increase in current density and anode-to-cathode distance somewhat increases the current efficiency but entails a higher voltage across the cell (V) and a greater energy consumption. Existing magnesium cells operate on a current density of 0.5 to 0.7 A/sq cm and with a cathode-to-anode distance of 6 to 9 cm.

The efficiency of the process also varies with the design, depth and maintenance of the cell.

The current efficiency usually is 80 to 85 per cent, and one kWh of energy will ordinarily produce 60 to 65 grams of metallic magnesium. The cell voltage is anywhere between 5.5 and 6.5 volts. It takes 4.2 to 4.5 tons of anhydrous magnesium chloride or 9 to 9.5 tons of anhydrous carnallite (45 per cent $MgCl_2$) to produce one ton of magnesium.

136. Cell Design and Practical Electrolysis

A successful cell should meet the following requirements:

- (a) it should have a high output for a small volume and working area;
- (b) it should consume little energy per unit weight of metal;
- (c) it should be convenient and safe to operate;

(d) it should provide for complete recovery of chlorine without appreciable dilution with other gases;

(e) it should be capable of operating without overhauls and shut-downs for a long time, i.e., it should be resistant to heat and the action of molten salts.

Existing cells are designed for a current of 50 to 70 kilo-amperes. This current generates enough heat to keep the electrolyte in a molten state. With big cells, some form of heat abstraction has to be devised.

Cells are usually rectangular in shape and hold several units, each unit consisting of an anode compartment, a diaphragm and two cathode plates.

The cell is built into a welded steel shell reinforced with stiffeners and is lined with dense firebrick. Current to the anode can be supplied either from above or sideways.

Fig. 227 shows a cell with current supplied sideways. The anodes are graphitised blocks led into the cell through a side wall and fully submerged in the bath. Fig. 228 shows a cell with top-mounted anodes. The advantages of the former type of cell are the lower working voltage (by 0.5 or 0.6 volts) and the longer service life of their anodes (a year or more), but the anodes can only be replaced with the cell stopped and the bath emptied. Top-mounted anodes can be replaced without prolonged shut-downs, but their service life is shorter.

Figs. 229 and 230 present sectional views through the anode and cathode compartments of a cell with top-mounted anodes. The anodes are made up of several graphitised bars each. The spacings between the bars are rammed with a mixture of graphite flour and soluble glass. Current to the anode unit is conducted by a copper bus held in place by bolts.

The joint between the anode and the cover of the anode compartment is packed with asbestos cord and luted. The operator should keep constant watch on the packing and replace it when necessary. Still, some air may find its way into the anode compartment through leaks in the packing, and the anodes heated to 700°C burn off fairly quickly.

The top ends of the anodes stick out of the cell and are also oxidised as they are heated to over 350°C. As a protection against oxidation, the anode tops are impregnated with orthophosphoric acid (H_3PO_4) which changes to glassy metaphosphoric acid when heated to 270-290°C. The metaphosphoric acid forms a thin protective coating on the anodes. At over 400°C, however, this film proves inefficient.

The cathodes are substantial bent plates (see Fig. 230). They have stiffeners as a measure against buckling. The plates have

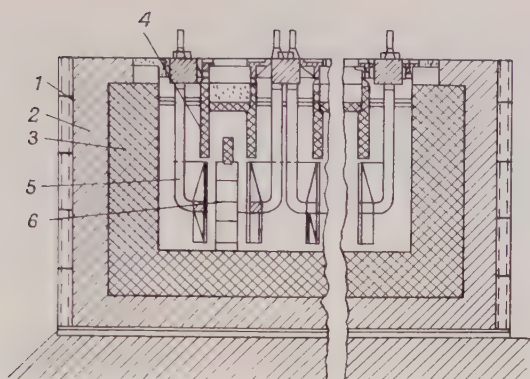


Fig. 227. Magnesium electrolytic cell with side-mounted anodes:
 1—shell; 2—thermal insulation; 3—lining; 4—diaphragm or hood; 5—cathode; 6—anode

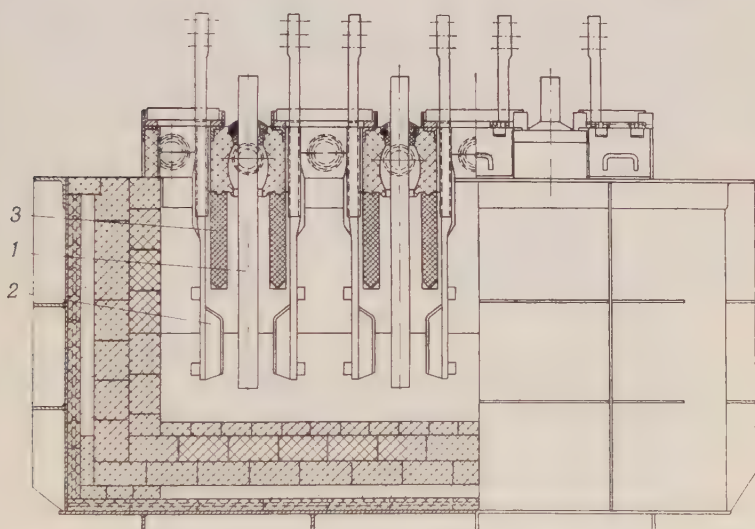


Fig. 228. Magnesium electrolytic cell with top-mounted anodes (sectional view):
 1—anode; 2—cathode; 3—diaphragm

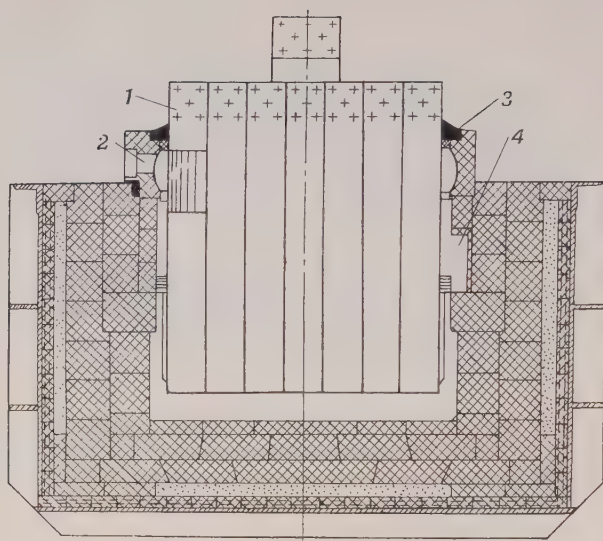


Fig. 229. Cross section through the anode compartment of a magnesium electrolytic cell with top-mounted anodes:

1—anode; 2—chlorine outlet; 3—asbestos seal at anode; 4—diaphragm

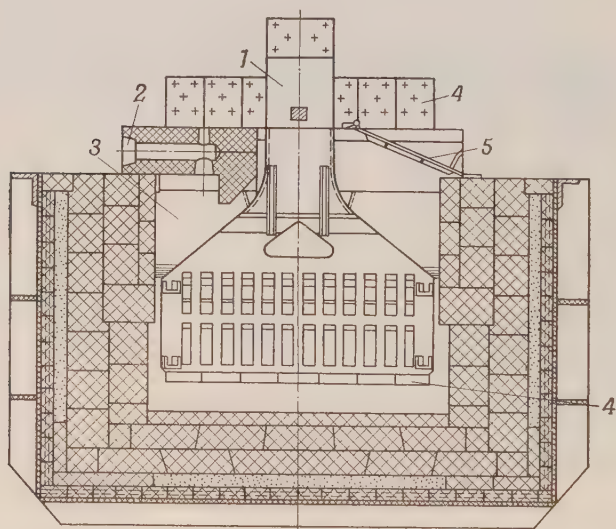


Fig. 230. Cross section through the cathode compartment of a magnesium electrolytic cell with top-mounted anodes:

1—cathode; 2—cathode gas outlet; 3—diaphragm; 4—anode; 5—lid

rectangular holes at the lower ends and a large triangular opening in the middle. The purpose of these openings is to equalise the composition of the bath and facilitate the transfer of globules of magnesium past the cathode.

The hot portion of the cathodes sticking out of the electrolyte is given a coat of lute as a protection against oxygen and chlorine.

The diaphragm operates under extremely adverse conditions and usually is a limiting factor both for the size and service life of the cell. The diaphragm must be strong, dense and resistant against oxygen, chlorine, molten chloride salts and temperature variations. These requirements are fulfilled by very dense high-quality grog.

The chlorine from the anode compartment is aspirated through the pipe 2 shown in Fig. 229. As it is recovered for the chlorination of magnesium oxide, care must be taken not to dilute the chlorine with air.

As the electrolyte circulates in the cell, some chlorine inevitably reaches the cathode space and also seeps through the hood. This calls for the aspiration of the gases from the cathode compartment as well, which fact considerably improves the atmosphere in the electrolytic shop.

Magnesium electrolytic cells usually operate for a year or so. At the end of this period the cell has to be shut down for the repair of the hood and sometimes lining. The anodes are replaced every eight or nine months. The cathodes can last for several years.

Magnesium electrolytic cells are connected in series of 60 to 100 units each. The number of cells in a series depends on the voltage of the source available and the cell voltage. The latter is in turn dependent on cell design, anode-to-cathode distance, bath composition and workmanship and usually ranges between 5.5 and 6.5 volts.

Cell Maintenance. Cell maintenance embraces (a) replenishment of the bath; (b) temperature adjustment; (c) removal of magnesium from the cell; (d) removal of the slime; and (e) care of the electrodes and contacts.

Replenishment of the bath. As electrolysis proceeds, more fresh magnesium chloride has to be added to the bath. There are several ways of doing this. For example, anhydrous carnallite may be added to the bath and some of the spent electrolyte withdrawn. Or molten magnesium chloride may be added in such a manner that its concentration in the bath never drops below 6 per cent. The addition of solid magnesium chloride would reduce the current efficiency by 3 to 5 per cent for the reason that anhydrous magnesium chloride, when cooled to below 600°C, eagerly absorbs moisture from the atmosphere.

Molten magnesium chloride at about 700°C is delivered to the cell from a chlorination furnace in closed ladles and is poured into the cathode compartment of the cell three or four times a day.

The magnesium chloride charged into the cell contains impurities which accumulate gradually in the electrolyte. If the bath composition is not to be upset unduly, it is good practice to remove some of the electrolyte from time to time. Each time a fresh charge of magnesium chloride is added to the bath, from 1 to 2 per cent the charge weight of finely divided and thoroughly dried fluorspar or sodium fluoride should be thrown directly into the bath.

Temperature adjustment. As has been noted elsewhere, the operating temperature of electrolysis should be 690 to 720°C. Any deviation from, especially an increase in, this temperature will impair the efficiency of the process.

As distinct from the electrolytic production of aluminium, the temperature is adjusted not by changing the anode-to-cathode distance but by varying the composition and, consequently, electrical conductivity of the bath. An addition of MgCl_2 , for example, will increase the resistance of the electrolyte, and the temperature of the process will rise. The temperature of the bath may be varied within 30 to 40°C by controlling the amount of gases aspirated from the cathode compartment.

Should the bath grow too hot, some solid anhydrous magnesium chloride may be added. If the temperature rise (or decrease) is due to the changed anode-to-cathode distance because of a bent cathode or a worn anode, the former should be removed and straightened or replaced. Should the bath grow too cold, as in the case of a shut-down, the cell may be started up by dipping Ni-Cr resistors into the bath and passing an alternating current through them.

Removal of magnesium from the cell. The magnesium is ladled out of the cell at least once a day. The accumulation of too much magnesium in the cathode compartment should be guarded against, because the metal may catch fire. No work can be done on a cell full of molten magnesium.

The molten magnesium is removed from a cell with Denisov (vacuum) ladles (Fig. 231). Before use the ladle 1 is heated by built-in heating elements 2 and carried to the cell by an overhead traveling crane. Then a vacuum of 550 to 600 mm Hg is built up in the ladle, a suction pipe 4 dipped into the cell, and its needle valve 3 opened. The molten magnesium and some electrolyte are aspirated into the ladle and the valve is closed. This cycle is repeated on all the cells until the ladle is full when it is disconnected from the vacuum line, and the electrolyte from the bottom portion of the ladle is returned to the process. The molten magnesium in the ladle is then taken to the foundry department.

Slime removal. The main ingredient of the electrolytic slime is the magnesium oxide which is added to the bath together with magnesium chloride and also comes from the hydrolysis of the electrolyte. Settling on the bottom, the magnesium oxide entrains other by-products and forms the slime.

In the case of magnesium chloride as the source material, the slime will have the following approximate composition: MgCl_2 ,

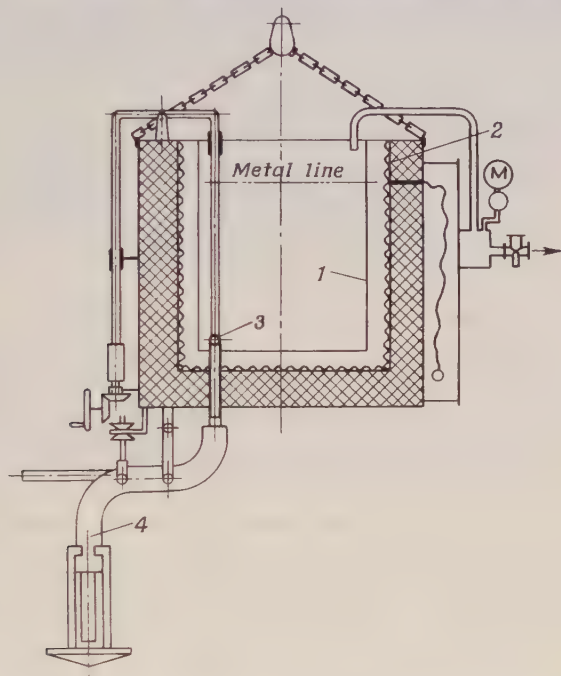


Fig. 231. Denisov vacuum ladle for removal of magnesium from electrolytic cells:

1—ladle; 2—heater; 3—stop valve; 4—suction pipe

5-10 per cent; MgO , 20-35 per cent; CaCl_2 , 30-40 per cent; $\text{NaCl} + \text{KCl}$, 10-15 per cent; $\text{SiO}_2 + \text{Al}_2\text{O}_3$, 1.5-2 per cent; and metallic magnesium, 2-3 per cent. Some 0.2 kg of slime is produced for every kilogram of magnesium. The slime is removed every other or third day, watching that it does not accumulate on the cell bottom, or else it may form a short circuit between the anode and cathode and hamper the deposition of magnesium on the cathode. The slime is removed with perforated skimmers by hand.

Care of the electrodes and contacts. Normal voltage across the cell terminals is between 5.5 and 6.5 volts. Poor contacts (especially

between the busbar and graphite anode) may however bring about a considerable rise in the cell voltage. The trouble may be easily detected by the heating of the contact surfaces or with the aid of a millivoltmeter. The contacts with increased resistance should be taken apart, cleaned and put together again.

An increase in the cell voltage may be due to the cathodes buckling away from the anode. It is a good plan, therefore, to withdraw the cathodes at least once in six to eight weeks and to straighten them. Sometimes, the cause of a voltage rise may be a thick and loose deposit of magnesium oxide and other compounds on the cathodes. The deposit results from some trouble in the composition of the bath. The slime-covered cathode should be immediately withdrawn and cleaned either mechanically or chemically. It is equally important to remove periodically the solidified crust of electrolyte from the walls of the anode compartment, since the aspiration of the chlorine may be handicapped.

137. Refining and Casting of Magnesium

Electrolytic magnesium usually contains about 5 per cent impurities which impair its mechanical properties and resistance to corrosion. Before it can meet the requirements of the relevant standard, electrolytic magnesium has to be refined (Table 54).

Table 54

Chemical Analysis of Refined Magnesium to U.S.S.R. Standard 804-56

Grade	Chemical analysis, per cent									
	Min. Mg	Max. impurities								
		Fe	Si	Al	Cl	Na	K	Cu	Ni	total
MF1	99.92	.04	.01	.02	.005	.01	.005	.01	.001	.08
MF2	99.85	.05	.03	.05	.005	.02	.005	.02	.002	.15

The impurities in electrolytic magnesium may be classed into two groups.

Group One embraces metallic impurities which find their way into magnesium during electrolysis. The principal among them are iron, sodium and potassium. Iron comes from the electrolytic decomposition of iron compounds. Sodium and potassium may be liberated from the bath under certain conditions together with magnesium.

Group Two covers non-metallic impurities mechanically entrained when the magnesium is ladled out of the cell. These are mainly CaCl_2 , MgCl_2 , NaCl , KCl and MgO .

Magnesium may be refined by fusion with fluxes or by retorting.

Fusion with fluxes. It is the most commonly used method of magnesium refining, but it is only efficient against non-metallic impurities. The flux used serves a twofold purpose: (a) it protects the metal from oxidation during smelting, and (b) it withdraws the impurities into the slag.

A variety of fluxes have been developed for magnesium refining. A typical flux usually contains salts of alkali and alkali-earth metals. One such flux developed by Krymov has the following composition: MgCl_2 , 40-46 per cent; KCl , 34-40 per cent; BaCl_2 , 5-8 per cent; CaF_2 , 3-5 per cent; $\text{NaCl} + \text{CaCl}_2$, not over 6 per cent; and MgO , not over 1.5 per cent. Generally, this flux yields good results.

The actual procedure of refining depends on the flux composition, smelting equipment and crude magnesium used.

When refining crude ingots, the procedure is this: ingots are charged into a crucible, melted and raised to 700 or 750°C; flux is added and thoroughly stirred into the molten metal; a more refractory flux is then introduced or fluorides are added to the one used before; the charge is again fused; and the molten bath is allowed to settle quietly at 710 to 690°C until a solidified crust of slag forms on the surface. The slag crust is broken up and the refined magnesium is cast into pigs.

Retorting. This method utilises the higher pressure of magnesium vapours in comparison with the vapour pressure of the impurities usually present in crude magnesium, such as iron, silicon, copper and aluminium. Some impurities have a higher vapour pressure than does magnesium. These are sodium and potassium. As will be recalled, chlorides of sodium, potassium, magnesium and calcium have a boiling point which comes closest to that of magnesium (Table 55).

Table 55

Boiling Points of Magnesium and Crude-magnesium Impurities

Pressure, mm Hg	Deg. C										
	Mg	Fe	Cu	Si	Al	Ca	K	Na	MgCl_2	KCl	NaCl
760	1107	2735	2595	2287	2560	1487	774	892	1418	1407	1465
0.076	516	1564	1412	1572	1110	688	261	340	—	704	743

Investigations show that the best results can be obtained from retorting in a vacuum at a temperature of about 600°C and a

residual pressure of 0.1 to 0.2 mm Hg. A convenient apparatus for this purpose has been developed by Verigin (Fig. 232). With this apparatus, retorting is a batch process. The apparatus consists essentially of a hermetically sealed retort. Its lower end is within a heating furnace and serves as a vaporiser. The top end is cooled and serves as a condenser. A vacuum is built up inside the retort. It is well-advised to build up some vacuum inside the furnace,

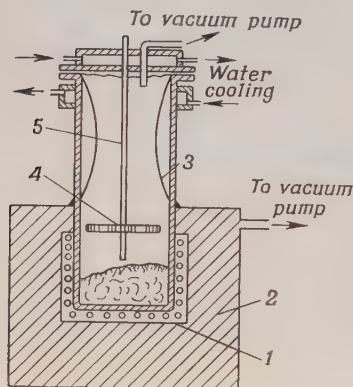


Fig. 232. Diagrammatic representation of vacuum furnace used to refine magnesium by retorting:

1—heater; 2—thermal insulation; 3—magnesium crystals; 4—shield; 5—thermocouple

too, so as to reduce the oxidising effect of the air and the pressure of the atmosphere on the hot part of the retort. At 450 to 500°C in the condenser, the magnesium settles on the walls in the form of bright clusters of crystals. The magnesium is the clearest in the middle portion; the crystals at the top may be contaminated by other volatile impurities while at the bottom they may carry some less volatile impurities. The crystals from the middle portion are separated from the rest, remelted and cast into the desired commercial form. The final product is 99.99 per cent or more pure.

Casting and ingot protection. Refined magnesium is cast into ingots, sticks, bars, etc., on a moving-belt casting machine. To protect the metal in the pouring ladle and moulds from oxidation, it may be sprinkled with powdered sulphur. When ignited, the sulphur burns to produce a protective blanket of sulphurous oxide.

Magnesium ingots intended for immediate consumption are cleaned of salt inclusions first mechanically and then by rinsing with a hot sodium-carbonate solution (20-50 g/litre of Na_2CO_3). Next the metal is washed in running cold water and oxidised with a weak hot solution of potassium bichromate. If magnesium ingots are to be shipped or held in storage, they are given a thin coat of a mixture of paraffin and petroleum jelly.

138. Economics of Electrolytic Magnesium Production

Table 56 gives a break-down of the cost of refined magnesium produced from a mixed bath of magnesium chloride and carnallite.

Table 56
Break-down of Cost of 1 Ton of Magnesium

Item	Share in total cost, per cent
<i>Direct materials</i>	
Artificial carnallite	10.0
Natural magnesite	2.0
Caustic magnesite	1.3
Oil coke	3.2
Coal pitch	1.3
	Total 17.8
Indirect materials	2.8
<i>Process fuel, heat and water</i>	
Coal or gas	3.0
Steam	0.4
Water	1.6
	Total 5.0
<i>Electricity</i>	
D.c.	25.5
A.c.	2.7
	Total 28.2
Wages of productive workers	14.6
<i>Departmental burden</i>	
Running repairs and depreciation	12.8
Other departmental expenses	12.2
	Total 25.0
Factory expense	6.6
	Factory cost 100.0

Referring to the table, the single largest element of cost is electricity. Power consumption may be reduced considerably by better and more efficient maintenance of the cells (by the use of the opti-

mum bath compositions, bath temperatures, and due care of the contacts in the d.c. circuit of the cell) and by using improved and bigger cells, non-buckling cathodes, etc.

The direct materials make up the second largest element of cost. This item may be reduced by using the materials sparingly.

Depreciation and running repairs also make up an appreciable item, mainly due to the fact that the cell has a short service life. This element of cost may be reduced by using stronger materials for the hood and lining and better methods for anode protection.

The cost of direct labour may be reduced by mechanisation and automation and through increased labour productivity.

139. Magnesium Reduction Processes

The complex and harmful nature of electrolysis for the production of magnesium has long spurred the search for other methods of magnesium production. The reduction of magnesium from magnesia which is in turn produced from widely occurring magnesite or dolomite has proved the simplest among them.

The first successful application of the magnesium oxide reduction process dates from the 30s. During 1940-45, two modifications of the process were in use, one based on carbon and the other on silicon as reducing materials.

The carbon reduction process. The reduction of magnesia by carbon may be pictured taking place as follows:



The equilibrium in this reaction depends on the equality of dissociation pressures

$$P_{\text{O}_2}(\text{MgO}) = P_{\text{O}_2}(\text{CO})$$

and on the pressure of magnesium vapours.

The shift of the reaction to the right, i.e., reduction, will only be possible if the dissociation pressure of magnesium oxide is higher than that of carbon oxide. Otherwise, the magnesium will be oxidised.

It has been shown previously that this method is used for the production of iron, nickel, lead, tin and other metals possessing a relatively low affinity for oxygen—a factor which makes their reduction by carbon possible at a point below their boiling points.

Oxides of light metals (aluminium, magnesium, etc.) have a strong affinity for oxygen and can therefore be reduced by carbon only at very elevated temperatures, usually well above their boiling points. This is the reason why light metals at the moment of reduction are in gaseous form.

Where a metal is reduced in a molten or solid state, it can be easily and conveniently separated from the gaseous products of the reaction, and their reoxidation on cooling is insignificant owing to the small surface area and low affinity for oxygen.

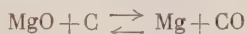
Where, on the other hand, a metal is reduced in gaseous state, it has to be cooled to below the dew point before it can be separated from carbon oxides. Unfortunately, the cooling of the gaseous mixture is accompanied by reoxidation of the evaporated metal.

This fully applies to the reduction of magnesium oxide by carbon. The equilibrium temperature below which magnesium vapours are reoxidised is about 1900°C and the dew point of magnesium is much below 1000°C. Consequently, before the reaction products can be separated, they should be cooled by more than 1000°C while being in a state of non-equilibrium. When cooled to below 1900°C, however, they will react with one another, and the magnesium vapours will be reoxidised by carbon monoxide.

There are several methods by which the reverse reaction can be checked, such as by diluting the products with a neutral gas, by suddenly cooling them to a temperature where the rate of reaction is low, or by absorbing the vapours of the reduced metal with some other molten metal.

The carbon reduction of magnesium oxide uses the rapid cooling of reaction products.

Several investigators have shown that magnesium and carbon monoxide react to an appreciable degree only at temperatures over 300°C. So, if the products of the reaction



are suddenly cooled to below 250°C, it is possible to obtain powdered magnesium in amounts varying with the rate of cooling. Satisfactory yields of metallic magnesium are possible by cooling from 2000 to 200°C within a few hundredths of a second.

Practically, the process is carried out as follows.

Magnesium oxide and oil coke are mixed in a definite proportion and the mixture is ground. The ground material is briquetted and charged into a suitable three-phase arc furnace. Fig. 233 shows a 8000-kW furnace. The reducing agent being gaseous hydrogen, the furnace is built into a hermetically sealed steel shell with a lid. The carbon supports 1 inside the shell carry carbon blocks 2 which enclose the melting chamber of the furnace. The blocks are held in place by arches and braces. The space between the lining and shell is filled with a thermal insulating material (which may be carbon black or pulverised coal). The melting chamber measures about 4 cu m in volume. The three graphite electrodes 500 mm in diameter are passed into the furnace through openings in the roof. Briquettes

are charged through two hermetically sealed hoppers in the furnace roof, feeders and a heat-resistant steel pipe the lower end of which is oil-cooled. After the top hopper is filled with briquettes, the air from it is swept out by nitrogen, and the briquettes descend into the lower hopper filled with hydrogen and into the pipe which admits the briquettes into the furnace.

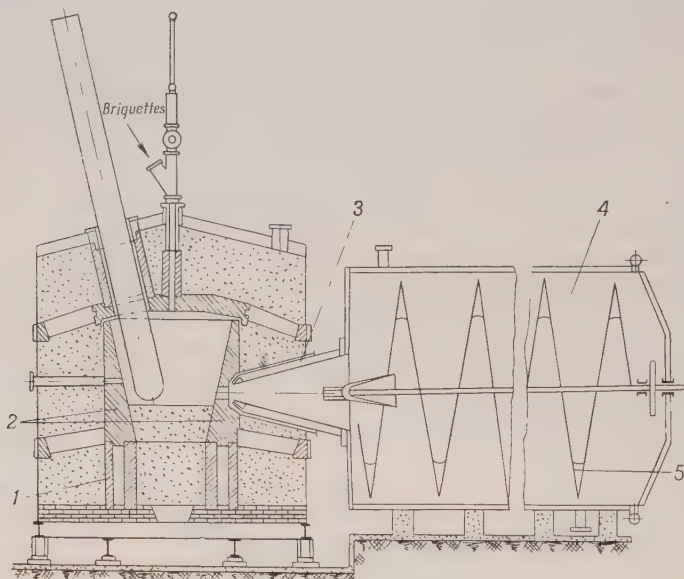


Fig. 233. Magnesium-reduction arc furnace

A very important part of the furnace is the cooling cone 3. The cone tip has to be as close as possible to the melting space of the furnace, and so it is made in heat-resistant steel. The cooling gas, which may be either purified hydrogen or natural gas, is admitted through the cone tip. From the cooling cone the gas carrying about 30 g/cu m of dust enters a cooler 4 measuring 10 metres in length and 4.6 metres in diameter and enclosed in a water jacket. In the cooler about 20 per cent of the magnesium dust settles and the gas is cooled to 120°C . The settled dust is discharged from the cooler by a screw feeder 5. The bulk of the magnesium dust is carried by the gases into a heat exchanger to be cooled to 80°C and trapped in a baghouse. The dust contains approximately 50 per cent metallic magnesium, 20 per cent carbon, and 30 per cent magnesia. The dust is briquetted and retorted to drive off metallic magnesium. The magnesium crystals thus obtained are then remelted. After

remelting the product is 99.97 per cent pure. Power consumption is about 21 kWh per kilogram of magnesium.

Magnesium reduction by silicon. If the reducing material is other than carbon, the reaction may be written as follows:



At the operating temperature only magnesium will be in vapour form—a factor appreciably facilitating magnesium production as there exist no complications of the carbon reduction process.

Whether or not a given material is capable of reducing magnesium depends on its affinity for oxygen. More specifically, any other metal can reduce magnesium oxide only if the free energy of formation of its oxide is greater than that of magnesia (see Fig. 107).

At low temperatures magnesia has a greater free energy of formation than do the oxides of other metals, and so it will reduce them and not vice versa.

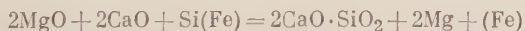
At elevated temperatures, on the other hand, aluminium and silicon will reduce magnesia, the former at not below 1750°C and the latter at not below 2300°C and normal pressure.

Aluminium is fairly expensive and has not found any use as the reducing material for magnesium while silicon, in addition to being cheaper, requires lower temperatures for the reduction of magnesia. This is because the silica produced in the process reacts with the other oxides to form silicates, and the free energy is additionally reduced by an amount necessary for the formation of $2\text{MgO} \cdot \text{SiO}_2$ and other silicates. In a general form, the reduction of magnesium oxide by silicon may be described as follows:



To avoid oxidation of magnesium vapours, the process must be carried out either in an inert atmosphere or in a vacuum. The latter method is more attractive, because it requires a lower temperature. In a commercial application, a residual pressure of 0.05 to 0.02 mm Hg makes it possible to maintain the temperature of the process at 1160 to 1170°C while in the case of atmospheric pressure the temperature would have to be kept at about 2000°C.

It is more advantageous to use dolomite and not magnesite as the source material for the process and the cheaper ferro-silicon instead of silicon as the reducing material. For such a case, the reaction will be



When enough calcium oxide is present, practically all the magnesium is reduced from the dolomite. The iron of the ferro-silicon does not take part in the reaction.

An addition of fluorspar can appreciably speed up the reaction and improve the recovery of the magnesium from dolomite with ferro-silicon. A few per cent of CaF_2 added to the charge increases the utilisation of the reducing material by 5 to 15 per cent and speeds up the reaction. An addition of calcium chloride acts in the same direction but to a lesser degree.

The industrial procedure of the silicon reduction process is fairly simple.

Calcined dolomite, ferro-silicon and fluorspar are ground, proportioned (in the proportion of 5 tons of dolomite to about 1 ton of ferro-silicon, or 75 per cent Si), and mixed. The charge is briquetted, the briquettes are fired and charged into tubular retorts cast of heat-resistant steel (Fig. 234). The retorts are heated at the closed ends fitting into a furnace, while the open ends serve as condensers. To facilitate condensation, the open ends of the retorts are water-cooled and split steel cylinders are inserted into them. Magnesium crystals settle on the walls of these cylinders. The condensers are screened from the charge by shields as a protection against the heat radiated by the hot charge. The retorts are fitted with tightly closed lids.

A typical furnace takes 20 retorts and can be heated with either gas, or liquid fuel, or electricity. Fig. 235 shows a cross-sectional view of the furnace.

The retorts operate intermittently, a working cycle lasting 10 hours. After a retort is cleaned of bicalcium silicate and iron, paper bags holding small briquettes are charged into it. The paper bags burn in a few minutes, the retorts are closed with lids, and the air is evacuated from them. The temperature is maintained anywhere between 1155 and 1175°C at a residual pressure of not over 0.1 mm Hg. If the magnesium crystals forming in the condensers are to be large and dense, the temperature in the retort should be 475 to 550°C. For a charge of 100 kg, the cycle occupies 9 to 9.5 hours. At the end of a cycle, the vacuum pumps are stopped, the lids lifted, and the magnesium crystals discharged for remelting. The final product is extremely pure. A single furnace holding twenty retorts produces 600 to 700 kg of magnesium per 24 hours.

The principal difficulty of the process is the low strength of the retort material. Retorts made from expensive Cr-Ni heat-resistant steel (28 per cent Cr and 15 per cent Ni) flatten after a run of 100 days. To extend their service life, they are repaired right in the furnace by pumping air into them. This expedient adds another 150 days to their service life.

The high cost of retorts has stimulated research work on other types of plant. Mention may be made of the drum furnace developed in Hungary (Fig. 236). The reduction space measures 500 mm in

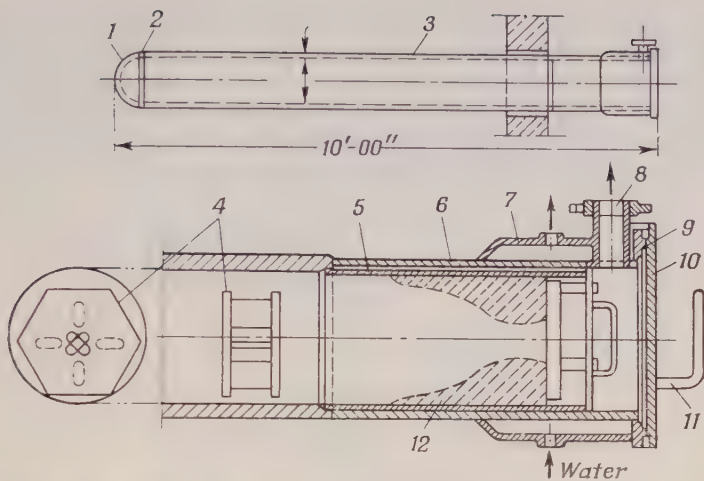


Fig. 234. Retort for the reduction of dolomite with ferro-silicon:

1—cast bottom; 2—welded joint; 3—cast pipe of heat-resistant steel; 4—radiation shield; 5—magnesium condenser; 6—seamless steel pipe; 7—water cooler; 8—connection to vacuum line; 9—rubber gasket; 10—lid; 11—handle; 12—magnesium crystals

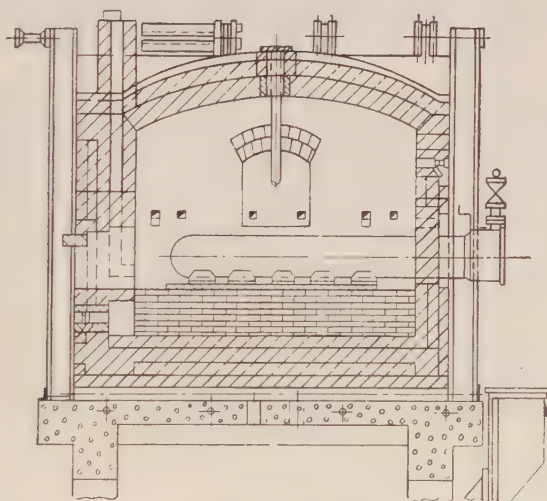


Fig. 235. Retort furnace for silicon reduction of magnesium (sectional view)

length and 500 mm in diameter. The furnace is lined with magnesite and grog. Heat is supplied by a carbon pipe 1 held in carbon sleeves 3 and 4. The carbon pipe has openings for escape of magnesium vapours into the condenser zone 2. Current is conducted by brushes 5 to a copper ring 6 insulated from the furnace shell. Flexible conductors 7 connect the ring with a water-cooled pipe 8 which terminates

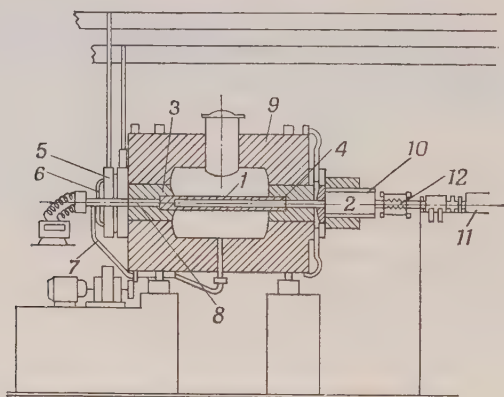
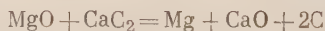


Fig. 236. Diagram of a Hungarian prototype magnesium reduction furnace

in a cone 8 of heat-resistant steel. The cone is held against the end of a resistor 1. The other end of the resistor is in contact with another current-conducting ring connected to the furnace shell. The shell 9 is carried by four rollers and rotates at a speed of 2 rpm. The rotation speeds up the heating of the charge and the rate of the reaction. The condenser 10 has thermal insulation which maintains the temperature in the condenser between 450 and 500°C. The vacuum line 11 is connected to the condenser by means of a seal 12.

Other thermal processes of magnesium production. Efforts are constantly made both to develop cheaper reducing materials and simpler apparatus for magnesium production by thermal processes. Mikulinsky and Darbinyan of the U.S.S.R. have proved the possibility of reducing magnesium by calcium carbide according to the reaction



Several types of apparatus have been developed for the silicon reduction of magnesium, using internal heating and dispensing with expensive heat-resistant alloys and other materials.

Speaking of the relative advantages of the silicon and carbon reduction of magnesium, preference ought to be given to the former process as being simpler and safer. The reduction of magnesium by carbon produces powdered magnesium which is explosive, while the sudden cooling of the products is an expensive and complicated operation. Yet, the carbon process firmly holds ground where powdered magnesium is the product sought for.

Thermal processes stand to win much if a method were developed by which magnesium vapours would be absorbed by a molten metal and then driven off by retorting.

Part Six

THE METALLURGY OF REFRACTORY METALS

Chapter XIX

THE METALLURGY OF TUNGSTEN

140. General

In appearance compacted tungsten resembles steel, while in powdered form it is of dark-grey colour. The metal has a body-centred cubic lattice and a specific gravity of 19.3.

Tungsten melts at 3400°C and boils at 5700°C.

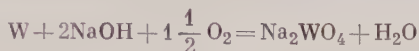
The mechanical properties of tungsten depend on the treatment it has been given. In hardness ($HB = 200-400$) and tensile strength (110-180) it comes close to hardened steel. The electrical and thermal conductivity of tungsten is one-third of copper's.

The electron configuration of tungsten is such that its valence may vary between 2 and 6, the latter being more characteristic of the metal. In aqueous solutions, it usually forms complex anions with oxygen and metalloids.

When cold, tungsten stands up well to the attack of concentrated and diluted mineral acids and aqua regia. When heated to 80-100°C it can only resist hydrofluoric acid, while other acids dissolve it to an appreciable degree. A mixture of nitric and hydrofluoric acids readily acts on tungsten.

The resistance of tungsten towards acids is due to the fact that the tungsten cations forming in aqueous solutions are unstable. On breaking up, they form complex anions of poorly soluble acids, such as H_2WO_4 . In hot alkaline solutions tungsten is less stable than in acids owing to the formation of readily soluble tungstates.

In the presence of oxidants, tungsten is easily attacked by alkalis, especially in molten form:



Atmospheric oxygen and water vapours oxidise tungsten at temperatures over 400 to 500°C. At 600 to 700°C oxidation results in the trioxide, WO_3 .

The lower tungsten oxides, WO_2 and W_2O_5 , are formed by the partial reduction of tungstic anhydride (or "anhydrous tungstic acid"), WO_3 .

From oxides, tungsten is usually reduced with hydrogen, since with carbon it forms carbides WC and W_2C , especially at temperatures over 1400°C. Heated to 2000°C, tungsten also reacts with nitrogen to form a nitride, WN_2 .

Although tungsten in powder form was first obtained in 1783, it was not until 1909 that it came into commercial use in connection with the manufacture of high-speed steels.

Over a half of the tungsten produced today goes to make high-speed and other special steels. Cutting, milling and other tools of high-speed steels have appreciably increased the rates of metal-working. The heat generated in the process does not impair the hardness and wear-resistance of the tools, even though maybe heated to a temperature of 650°C. Along with tungsten, high-speed steels contain additions of chromium, nickel, vanadium and cobalt.

Added to a steel together with other alloying elements (Cr, Ni and V), tungsten makes the steel self-hardening and raises the permissible temperature to 700-900°C.

Tungsten and tungsten-cobalt alloys have excellent magnetic properties and are widely used in the manufacture of permanent magnets for radio and electrical applications.

Alloys of tungsten, tantalum, niobium, molybdenum and rhenium retain their full strength at extremely elevated temperatures and are used in the fabrication of components for jet planes and missiles.

Apart from its role as an alloying addition, tungsten is widely employed in the form of tungsten carbide, WC . Tungsten carbide is a crystalline material approaching diamond in hardness. Bonded by cobalt powder, tungsten carbide is made by methods of powder metallurgy and sintering into sintered or cemented carbides. The

usual composition of sintered carbides is 85-90 per cent WC, 5-15 per cent Co and, sometimes, carbides of titanium, tantalum and niobium (columbium). Sintered carbides make excellent drills, milling cutters, drill-bits and wire dies which retain cutting properties up to 1000 or 1100°C. Sometimes, many of these applications use cast tungsten-carbide alloys.

Pure metallic tungsten remains the best material for the filaments of incandescent lamps and radio valves.

This is because tungsten is very durable in a vacuum or in an atmosphere of inert gases, such as helium, neon, argon, and krypton, at temperatures up to 2500°C.

Alloys of tungsten, cobalt and chromium are used for hardfacing punches, turbine vanes, aircraft engine valves and other wearing parts as a protection against wear and attrition.

Compound contact metals made by incorporating copper, silver or gold with tungsten possess high electrical conductivity and excellent wear resistance under conditions of sparking or arcing and so go to make switches, circuit breakers and other switch gear.

Sodium tungstate (Na_2WO_4), tungstic acid (H_2WO_4) and some other compounds of tungsten find uses in the manufacture of textiles, dyes, varnishes, leather and also in printing.

141. Sources of Tungsten

Tungsten minerals of commercial importance can be divided into two groups: the wolframite group which forms a continuous series of iron-manganese tungstates of the type $x\text{FeWO}_4 \cdot y\text{MnWO}_4$; and the scheelite group embracing the only mineral, scheelite, which is calcium tungstate (CaWO_4).

Tungsten ores often carry 0.3 to 0.5 per cent WO_3 . Ordinarily they form veins in quartzites or occur at the interface between granites and limestone. The weathering of parent igneous rocks leaves placers of tungsten ores.

The associates of tungsten in ores are tin as cassiterite, and also minerals of molybdenum, bismuth, arsenic and copper.

Wolframite ores are dressed by gravity concentration and magnetic separation, and scheelite ores by flotation. The resulting concentrates contain 40 to 70 per cent WO_3 .

Here are the typical results of tungsten ore concentration, in per cent:

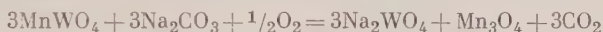
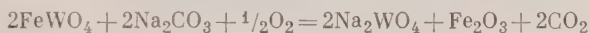
WO_3	40-70	Sn	0.03-1.5
MnO	0.008-18.0	As	0.01-0.05
SiO_2	5-10	P	0.01-0.11
Mo	0.008-0.25	Cu	0.1-0.22
S	0.5-4		

Sometimes tungsten concentrates are additionally roasted to remove the sulphur and arsenic and treated with an acid to eliminate the iron and other impurities. Acid treatment is also resorted to in order to remove the iron oxide film from non-magnetic minerals prior to magnetic separation.

142. Treatment of Tungsten Concentrates

Different methods are employed for the treatment of wolframite and scheelite concentrates. The first stage, however, in both cases is to break down the concentrate so that the tungsten may be converted to easily soluble chemical compounds.

Breakdown of Wolframite Concentrates. Wolframite concentrates are usually broken down by roasting or fusion with sodium carbonate, when the following reactions take place:



Roasting is done at 800 to 850°C and fusion at 900 to 1000°C. In the case of fusion, and additional oxidant (ammonium nitrate or sodium chlorate) is used to make up for the lack of oxygen in the charge.

Some concentrates can be successfully broken down with a solution of sodium hydroxide at about 100°C to form sodium tungstate according to the reaction



This process is cheaper and simpler, but cannot be applied to all grades of wolframite ores.

Roasting or fusion with sodium carbonate, when done on a limited scale, is carried out in reverberatory furnaces with a hearth area of 6 to 8 sq m, burning fuel oil or gas. The charge is composed of tungsten concentrate, sodium carbonate (with an excess of 10 to 15 per cent above the combining amount) and, where necessary, a small amount of nitre. The roasted product is rabbled out of the furnace by hand; the fused product is run off from the furnace while liquid. The operation requires two to three hours to complete.

Where large quantities of concentrate have to be treated, use is made of rotary kilns similar in design to those employed to calcine bauxites or alumina (see Fig. 177). They measure up to 20 metres in length and about 2 metres in diameter. They can handle as much as 25 tons of charge a day.

The cooled mass from the furnace, after being crushed, is treated for the extraction of sodium tungstate with water under agitation

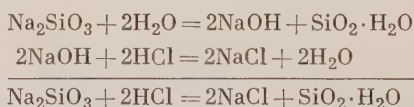
and a temperature of 70 to 90°C. Counter-current leaching done in two or three steps may produce a solution of sodium tungstate containing 200 to 270 grams per litre of tungsten trioxide.

At large plants using continuous calcination, the fused material is crushed and leached in drum digesters, similar in construction to rod mills (Fig. 237).

The insoluble residue is separated either by filtration or counter-current decantation in a system of settling tanks. Pulps with a high liquid-to-solid ratio should be preferably passed through filter-presses such as described in the metallurgy of zinc, while thick pulps may be treated in intermittent vacuum filters. The tailings are washed to not over 0.02 or 0.03 per cent of water-soluble tungsten. If the total tungsten in the tailings is high, they are re-treated for the additional recovery of the value.

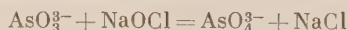
The solution of sodium tungstate is finally purified to eliminate its silica, arsenic, phosphorus and molybdenum.

Removal of silica. Silica is present in the sodium tungstate solution as sodium silicate. Its removal is based on the hydrolysis which is induced by an addition of hydrochloric acid, since this decreases the pH value to 8 or 9. The sodium silicate is decomposed to form silica gel:



The hydrolysis of sodium tungstate with the formation of the insoluble H_2WO_4 can only begin at pH 2. Hydrochloric acid should be poured into the hot sodium tungstate solution in a thin jet, while vigorously stirring the solution. After boiling and settling, the residue of silica is filtered off.

Removal of arsenic and phosphorus. Their removal is based on the formation of poorly soluble magnesium salts of arsenic and phosphoric acids. Prior to precipitation, the arsenite is oxidised to arsenate with sodium hypochlorite:



Then magnesium chloride is added to the solution which is boiled for three or four hours and filtered to remove the residue consisting of $\text{Mg}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{AsO}_4)_2$.

The removal of arsenic and phosphorus is more complete when ammonia or an ammonium salt is simultaneously added to the solution and the latter is allowed to settle for a long time. As a result, still less soluble double salts of magnesium and ammonium $\text{MgNH}_4(\text{PO}_4)$ and $\text{MgNH}_4(\text{AsO}_4)$ appear in the residue.

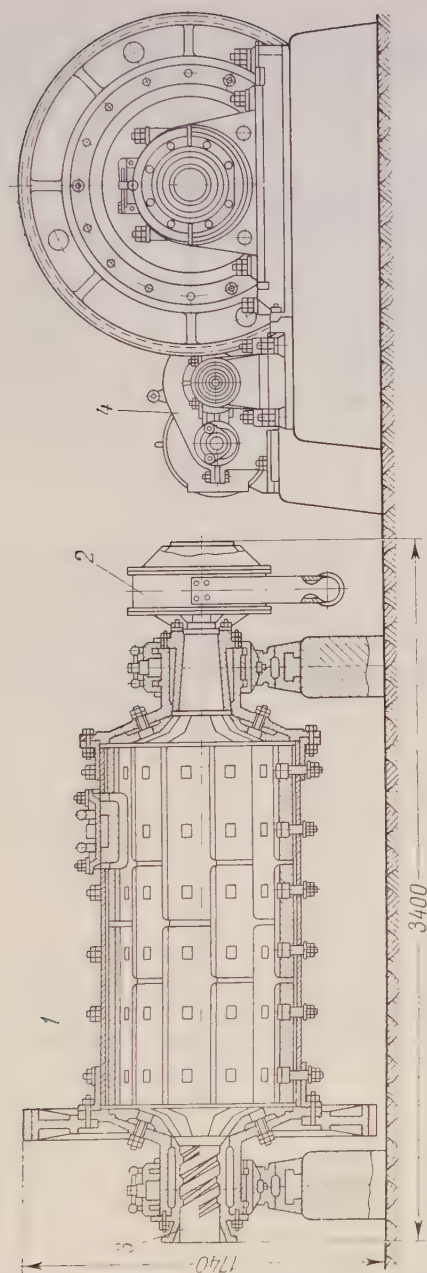
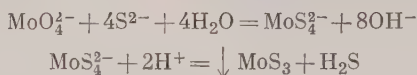


Fig. 237. Drum-digester for continuous leaching of sinter;

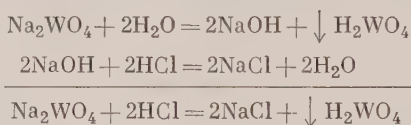
1—steel drum lined with hard-steel wearing plates; 2—volute feeder; 3—discharge trunnion; 4—gearbox and motor

Removal of molybdenum. This treatment is effected by adding sodium sulphide to fix the molybdenum before the tungsten into a soluble thiosalt. The hydrochloric acid is added to the solution and molybdc sulphide, MoS_3 , is precipitated according to the reaction



In this operation control must be held within very narrow limits, for under improper control tungsten is also precipitated, thereby causing some loss of the metal.

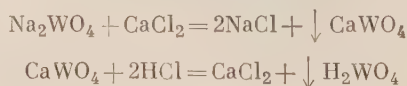
Precipitation of tungstic acid. If hydrochloric acid is added to the solution of sodium tungstate, a yellow precipitate of tungstic acid is obtained:



A coarse-grained precipitate easy to filter off is obtained by running the sodium tungstate solution into the boiling hydrochloric acid which also contains some nitric acid or saltpetre. Nitric acid prevents the partial reduction of tungsten to pentavalent form which produces under these conditions readily soluble compounds.

Precipitation is carried out in vessels lined with rubber or acid-proof tile and fitted with mechanical stirrers. The residue is given repeated washing by decanting it six to eight times. An addition of hydrochloric acid or ammonium chloride to the wash water speeds up settling and prevents the formation of a colloidal tungstic acid which tends to absorb impurities.

If the tungstate solution carries a great deal of impurities or a coarse-grained precipitate is sought for, precipitation is conducted so as to obtain calcium tungstate as an intermediate product by adding sodium tungstate, calcium chloride or milk of lime to the solution. The operation is carried out under agitation in boiling solution containing 0.3 to 0.6 per cent free alkali. After repeated decantation with hot water, a thick mass appears in the residue. The pasty precipitate is then digested with hot hydrochloric acid under agitation and with live steam. The whole operation may be described by the following equations:



The precipitate is washed in the same way as in direct precipitation. As a coarse-grained material is obtained, washing requires less time and is more thorough.

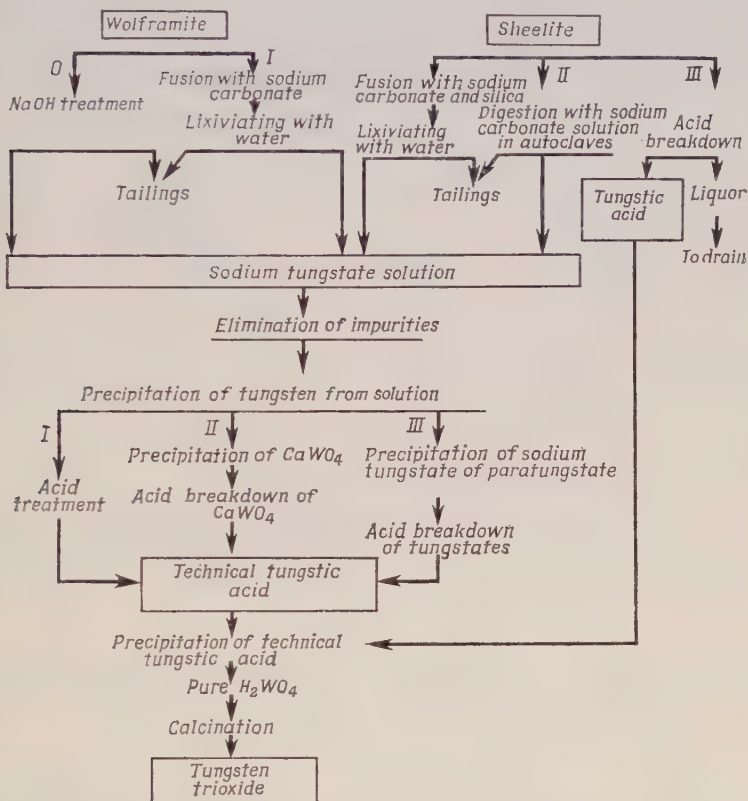


Fig. 238. Flow-sheet for production of tungsten trioxide from wolframite concentrates

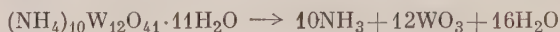
Purification of technical tungstic acid. The tungstic acid precipitated from a sodium tungstate solution directly or as calcium tungstate is a technical product containing 99.2 to 99.5 per cent WO_3 , calling for additional purification. In some cases, the product is sufficiently pure for the manufacture of cemented carbides; then additional purification may be dispensed with.

The most practical method is to dissolve tungstic acid in ammonia to obtain ammonium tungstate. The impurities iron, man-

ganese, aluminium and silica, remain in the residue and can be conveniently filtered off. An addition of acid to the solution throws down tungstic acid. A more complete purification is effected by digesting the ammonium tungstate so that it crystallises out as paratungstate, $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 11\text{H}_2\text{O}$.

Paratungstate comes from the partial hydrolysis of $(\text{NH}_4)_2\text{WO}_4$ due to the careful addition of acid to the solution or to the removal of some ammonia by evaporation. The solubility of ammonium paratungstate in water at 70°C is 79.4 g/litre, while at 17°C it is 0.64 g/litre. The largest crystals are produced by the slow cooling of the solution. The remaining tungsten is separated out of the mother liquor as H_2WO_4 or CaWO_4 and is returned to the previous stages in the process.

Upon evaporating to dryness, the ammonium paratungstate yields anhydrous tungstic acid:



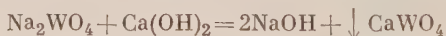
In some cases, the ammonium paratungstate is first decomposed by hydrochloric acid with the formation of tungstic acid in the residue.

A flow-sheet for the breakdown of wolframite concentrates is shown in Fig. 238.

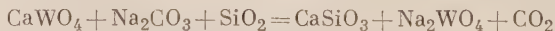
Breakdown of Scheelite Concentrates. Roasting with sodium carbonate could be applied to scheelite in order to transform it into sodium tungstate:



The subsequent leaching, however, would again produce some calcium tungstate which would appear in the residue:



As a result, the yield of tungsten would be insufficient. For these reasons, industrial practice is to roast scheelite with a mixture of sodium carbonate and quartz sand in which case the calcium forms a poorly soluble silicate:



But, again, an excess of sodium carbonate has to be added to make the recovery of tungsten more complete.

The subsequent stages: purification of the tungstate solution, precipitation of H_2WO_4 and its purification, do not differ from the respective steps in the case of wolframite.

Very rich and very pure scheelite concentrates may be directly broken down by hydrochloric acid into technical tungstic acid in a single operation.

Poor and low-grade scheelite concentrates can be successfully broken down by the autoclave-soda process developed by Maslenitsky and Syrokonsky. In this process, the concentrate is completely broken down by a solution of soda heated to 180–200°C in an autoclave at a pressure of 15 atmospheres (abs.). The amount of soda required is 3.5 to 4 times the WO_3 content in the ore by weight. The recovery of tungsten is up to 98 per cent.

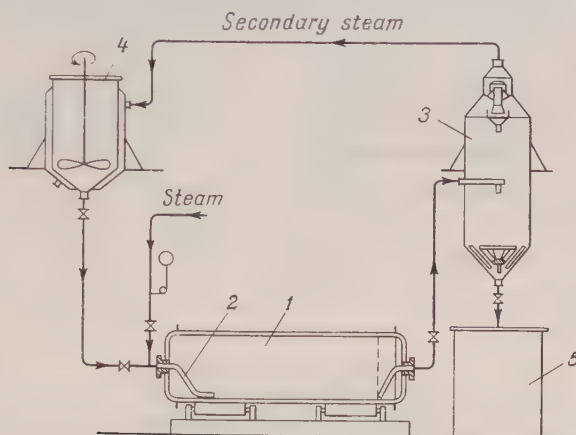


Fig. 239. Autoclave unit for leaching of scheelite concentrates:
1—autoclave; 2—tube to feed pulp and steam; 3—steam separator; 4—pressure vat for pulp; 5—leached pulp collector

Horizontal autoclaves operate intermittently. After leaching the pulp is directed into a steam separator (Fig. 174). The steam thus recovered is utilised to preheat the pulp. An autoclave plant is shown diagrammatically in Fig. 239.

Production of Tungsten Trioxide. Anhydrous tungstic acid is obtained from H_2WO_4 or ammonium paratungstate by calcining them. The temperature depends on the desired grain size of the product.

Ammonium paratungstate decomposes at a temperature of 250°C, and tungstic acid at 750–850°C. These products are calcined in small-size electric-heated rotary tube furnaces with cylindrical jackets of stainless steel (Fig. 240). The flue gas carrying mainly steam is passed through a bag filter. The grain size of the anhydrous tungstic acid thus obtained depends on the temperature in the furnace. Since the grain size has a marked effect on the subsequent production of tungsten metal powder, it is regularly monitored by measuring the bulk weight of, or the absorption of methanole vapour by, anhydrous tungstic acid in a suitable tester.

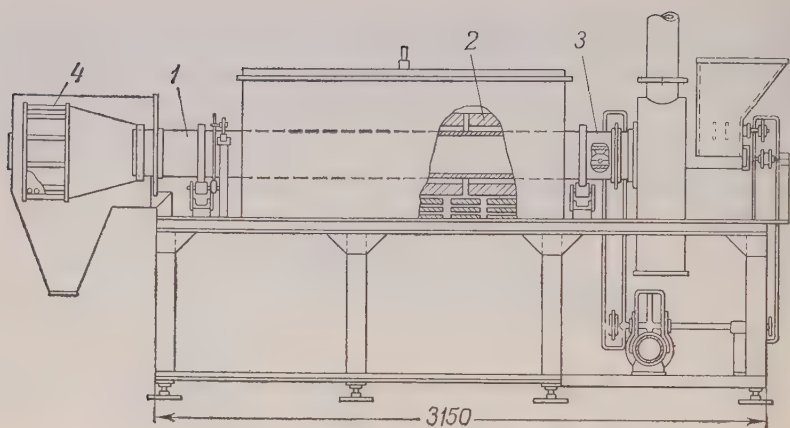


Fig. 240. Tube furnace for calcination of tungstic acid and ammonium paratungstate:

1—steel tube; 2—heating chamber with Ni-Cr resistors; 3—auger feeder; 4—drum sieve

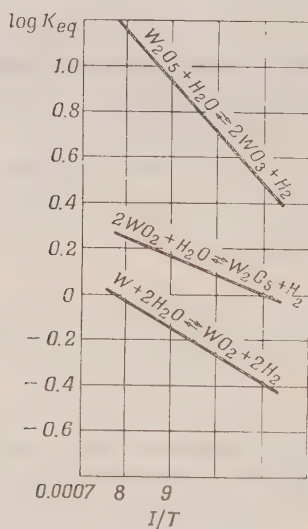
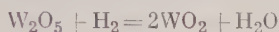
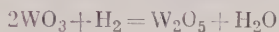


Fig. 241. Equilibrium curves for the reduction of tungsten oxides by hydrogen

143. The Production of Tungsten Metal Powder

Tungsten metal powder may be obtained by reduction of tungstic oxide with hydrogen or carbon.

Reduction with hydrogen. Three stages may be differentiated in the reduction of tungstic oxide with hydrogen:



The equilibrium constant for each stage is

$$K_{eq} = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

The respective equilibrium curves are shown in Fig. 241. Every next stage requires a higher temperature and a greater hydrogen content in the gas mixture.

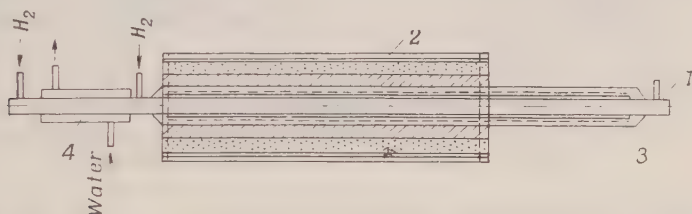


Fig. 242. Tube furnace for the reduction of tungstic oxide by hydrogen:
1—tube; 2—shell; 3—Ni-Cr resistor; 4—cooler

Commercially, anhydrous tungstic acid is reduced in a tube furnace (Fig. 242). The steel tube of the furnace is either gas or electrically heated over a portion 2 metres long. The tube is 50 to 100 mm in diameter. The material is loaded into nickel boats and stoked counter-current to the flow of the hydrogen. As the material travels through the furnace, it passes through the zones of increasing temperature and ever drier hydrogen until it arrives at the discharge end where a cooling zone is installed to prevent the tungsten metal powder from emerging hot. The maximum temperature is 850° to 860°C.

The hydrogen required for the process is supplied by the electrolysis of water in cells with iron or nickel electrodes and a caustic alkali electrolyte.

Before it is admitted into the furnace, the hydrogen is purified of oxygen by passing it through a red-hot copper mesh or platinated asbestos. Then the hydrogen is dried with soda lime, calcium chlo-

ride or silica gel; the remaining moisture is removed by phosphoric anhydride. After it leaves the reduction tube, the hydrogen is again circulated through the system after purification and drying.

The output of tube furnaces depends on the capacity of the boats used and their rate of travel through the tube. The higher the rate of travel, the coarser the tungsten powder. An ordinary boat holds 50-180 grams and travels at 50-180 cm/h.

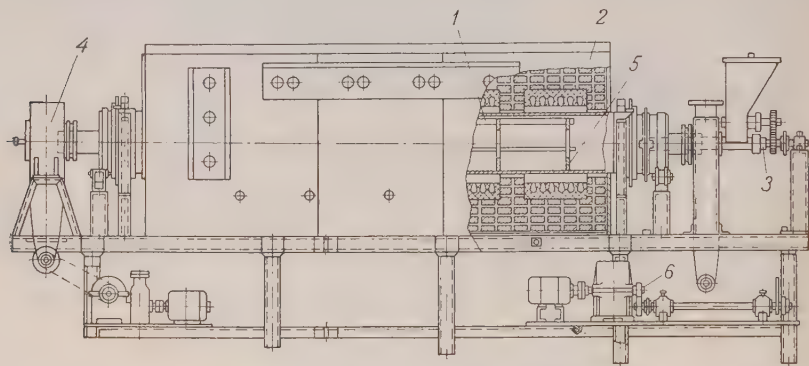


Fig. 243. Tube furnace for the reduction of anhydrous tungstic acid with hydrogen:

1—steel tube; 2—heating chamber; 3—feeder; 4—discharger; 5—perforated discs interconnected by steel shelves; 6—motor and gearbox.

Reduction of tungstic oxide is carried out in two stages. The first stage produces the brown oxide, WO_2 , at 720°C . The brown oxide is mixed with a fresh charge of yellow oxide, WO_3 , for the second reduction at 860°C .

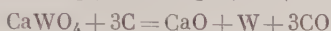
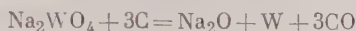
Multiple-tube (say, eleven-tube) furnaces are more efficient. All tubes are arranged in parallel in a common chamber heated by nichrome heating elements.

Some of the large plants in the Soviet Union reduce anhydrous tungstic acid in rotary tube furnaces with jackets of stainless steel, up to 4 m long and about 40 cm in diameter (Fig. 243). The jacket is heated by an electrical heating element from the outside. In the inside, the jacket is packed with perforated discs interconnected by steel angles. This arrangement prevents the charge from shifting too fast down the jacket and improves contact between the material and the counter-current of hydrogen.

Reduction with carbon. This process, although simple and cheap, may only be used where the presence of carbon in the tungsten does not run counter to the user's specifications. The carbon used for the reduction may be in the form of lampblack or sugar coke, which are both low in ash.

Industrially, the process is carried out at 1400-1800°C either in electrically heated tube furnaces with the reduction tube made of graphite or carbon, or in graphite crucibles. Since the metal produced by this method is always contaminated with carbide, it is only suitable for the manufacture of tungsten carbide alloys.

Tungstates may be reduced directly, without converting them into anhydrous tungstic acid, as follows:



The sodium oxide from the products of reduction is removed by washing in water, and the calcium oxide by tabling. The product thus obtained is only suitable for alloying with steel and some other metals.

144. The Manufacture of Ductile Tungsten

Ductile tungsten in wire and sheet form is solely manufactured from the tungsten metal powder reduced by hydrogen. The powder should have not more than 0.05 per cent impurities and most of the particles should be between 2 and 3 microns, the limits being 0.5 and 6 microns.

The manufacture of ductile tungsten (filament wire and sheet) consists of the following successive operations:

- (1) Pressing.
- (2) Presintering, or baking.
- (3) High-temperature sintering.
- (4) Treating.
- (5) Swaging.
- (6) Wire drawing.
- (7) Sheet rolling.

Pressing. The metal powder is loaded into a steel mould and subjected to a pressure of 2.5 to 3 tons per sq cm. To reduce friction between the mould walls and the material, a mixture of alcohol and glycerin or a solution of paraffin wax in petrol is incorporated into the powder. These additives also add strength to the bar for handling. The pressed bar is rectangular in cross section, with a base 10 mm square and 60 cm long.

Sintering. The pressed bar is too fragile to be handled safely. Therefore, it is heated in a hydrogen atmosphere, first for 20 minutes at 850-900°C (presintering or baking) and then for another 40 minutes at 1300°C (or high-temperature sintering). The hydrogen reduces the oxide films on the surface of the powder particles; at the same time, the bar shrinks, and its crystals grow in size.

Treating. This operation consists in heating sintered bars to a temperature close to the melting point of tungsten, i.e., 3000-3100°C,

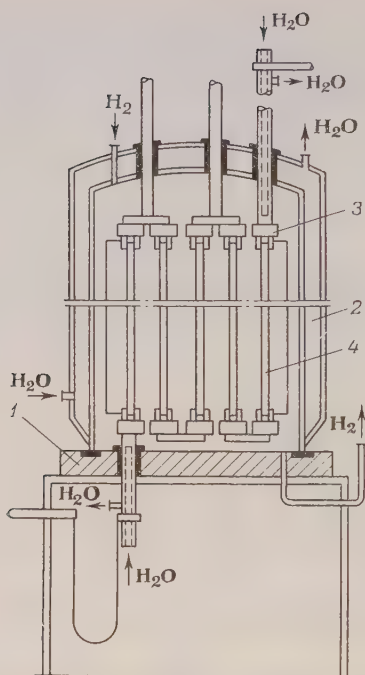


Fig. 244. Apparatus for treating sintered tungsten bars:
 1—bedframe; 2—water-cooled hood; 3—water-cooled contacts; 4—bars

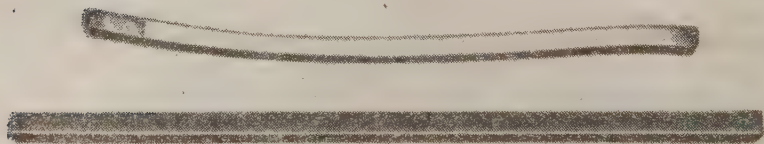


Fig. 245. Pressed (above) and sintered (below) bars of tungsten

by passing current through them. For this treatment the sintered bars are suspended from a water-cooled copper clamp so that their lower ends are clipped by another water-cooled clamp. This arrangement (Fig. 244) is set up on a steel slab and enclosed in a water-jacketed hood. The space under the hood is filled with hydrogen. Alternating current to the clamps is conducted at 10 to 15 volts.

Six to eight sintered bars are loaded into an apparatus for treating sintered tungsten at a time. The bars are connected so as to form a series electric circuit.

The treating schedule is determined by trial and error. First the amperage required to fuse the bar is determined. Then the current

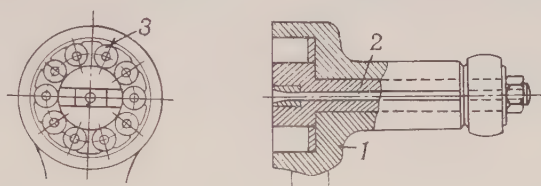


Fig. 246. Diagrammatic representation of a swaging machine:

1—housing; 2—shaft; 3—rollers

is raised during five or six minutes to 80 per cent of the fusing value, and the bar is held at this current for 10 minutes. Then the current is rapidly raised to 90 per cent of the fusing value and the bar is held for another 12 minutes. During the next one minute or two the current is gradually reduced and finally turned off. The treated bar (Fig. 245) has a density of 17.5 to 18.5 g/cu cm and a porosity of 10-15 per cent.

Swaging. After the above operation, the bar is strong but very brittle at ordinary temperature, and may only be hammered or rolled at 1200-1300°C in a hydrogen atmosphere.

For the production of wire, the treated bar is hammered in a swaging machine. A diagrammatic drawing of a swager is shown in Fig. 246.

The swager consists of a cast-iron cylindrical housing with a ring of steel rollers inside it. Passing through the centre of the housing is a shaft with a central bore for the bar and slots for the swaging dies of high-speed steel. The two halves of the die, which are rotated rapidly about the tungsten bar, fly apart by centrifugal force and are returned by the impacts from the surrounding ring of rollers. In a twelve-roller swager, the bar rotating at about 1000 rpm will receive 12,000 blows per minute. As it is customary to reduce the bar diameter a little at each pass, many passes and many

dies are required to reduce it to about 2 mm, when swaging may give way to wire drawing. The swaging operation begins at 1350 and is finished at 1200°C.

Wire drawing. Further size reduction to 0.3 mm is done by means of drawing through dies of tungsten carbide, while size reduction to 0.01-0.015 mm is through diamond dies. Wire less than 0.01 mm in diameter is manufactured by etching in molten saltpetre.

Sheet rolling. Plates and contacts for vacuum tubes are hot-rolled from tungsten bars in rolls of high-speed steel.

Chapter XX

THE METALLURGY OF MOLYBDENUM

145. General

Molybdenum resembles tungsten in appearance, crystalline structure and many other properties. Its specific gravity is 10.3. It melts at 2625°C and boils at 4700°C.

The mechanical strength ($HB = 150-250$; tensile strength = 140-260 kg./sq mm), electrical and thermal conductivities of molybdenum are lower than those of tungsten.

Both tungsten and molybdenum have similar electron configurations, the only difference being that the latter has a single electron in the outer shell and 13 electrons in the previous shell. Therefore, it may be expected that molybdenum can form compounds in valences from 1 to 7. In aqueous solutions, however, molybdenum is practically always hexavalent and is present in the form of oxygen-bearing anions MoO_4^{2-} or any other complex anions. Like H_2WO_4 , molybdic acid, H_2MoO_4 , is little soluble in water.

Molybdenum is less resistant against acids than is tungsten. When heated, it readily dissolves in nitric acid and aqua regia. Alkalis act on molybdenum much as they do on tungsten.

The highest oxide, MoO_3 , is formed by the oxidation of molybdenum by atmospheric oxygen or water vapours at 600-700°C. Below 400-500°C molybdenum is practically inoxidable.

Molybdenum trioxide has a relatively low melting point (795°C) and boiling point (1155°C) for which reason it is fairly volatile.

Molybdenum metal was first obtained in 1792 but it was not until the beginning of the current century that it came into industrial use.

Approximately 75 per cent of the molybdenum produced is used in ferrous alloys, including heat-resisting, tool, structural, stainless and acid-proof steels containing chromium, nickel and vanadium in addition to molybdenum.

Added to cast iron, molybdenum improves its resistance to wear and the action of hydrochloric acid. One such grade of silicon-molybdenum iron, known under the proprietary name of Antichlor, contains 3.5-4 per cent Mo.

Molybdenum is used as an addition to high-temperature alloys (superalloys) based on nickel, cobalt and chromium. Its alloys with the same metals and iron are acid-resistant and stand up well to the attack of mixed mineral acids, except hydrofluoric acid.

The pure metal in wire form is used in resistors for high-temperature electric furnaces, hooks for tungsten filaments in lamps, and in sheet form 0.1 to 0.2 mm thick as electrodes for radio valves and targets for X-ray tubes.

Pure molybdenum and molybdenum-base alloys retain their full strength at extremely elevated temperatures and are used in the manufacture of jet engines and missiles.

Sodium molybdate, Na_2MoO_4 , is used in the production of pigment colours for printing inks, lacquers and paints.

Molybdenum oxides are employed as catalysts in the hydration of coals and petroleum.

146. Sources of Molybdenum

Of the known molybdenum minerals, only molybdenite, a molybdenum sulphide, MoS_2 , is of commercial importance: about 99 per cent of the molybdenum produced is obtained from molybdenite ores.

Some ores also carry other molybdenum minerals, such as powellite (CaMoO_4), molybdite ($x\text{Fe}_2\text{O}_3 \cdot y\text{MoO}_3 \cdot z\text{H}_2\text{O}$), and wulfenite (PbMoO_4).

The associates of molybdenum in ores are often tin, tungsten, arsenic, copper and bismuth; but only copper is present in amounts sufficient for commercial recovery. Such ores are known as copper-molybdenum ores.

The gangue of molybdenum ores consists of quartz, cericite and fluorite. The ores occur as nests or veins in quartzites and also form shots.

Molybdenum ores are mainly concentrated by flotation. MoS_2 is easily floatable and its recovery into concentrates reaches 90 per cent. Rich concentrates contain up to 50 per cent Mo. Complex ores containing but a few hundredths of one per cent Mo give low-grade concentrates contaminated by copper and other impurities; still, they are commercial sources of molybdenum.

Ordinarily, molybdenum concentrates have the following composition: Mo, 47-50 per cent; P, 0.07-0.15 per cent; As, 0.07 per cent; Cu, 0.5-2.0 per cent; SiO_2 , 5-7 per cent; and Sn, 0.07 per cent.

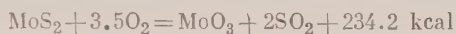
Molybdenite often carries rhenium as an isomorphic impurity in amounts as little as 0.0004-0.02 per cent. Still molybdenum ores are the main source of this rare metal.

147. Conversion of Molybdenum Concentrates

Molybdenum is manufactured in much the same way as is tungsten: concentrates are first treated to obtain molybdenum trioxide called anhydrous molybdic acid; the trioxide is reduced by hydrogen to give the molybdenum metal powder which is fabricated into

compact ductile molybdenum exactly as tungsten is; the ductile rods are drawn into wire or rolled into sheet. The other marketable forms of molybdenum are ferro-molybdenum, anhydrous molybdic acid, molybdic acid H_2MoO_4 and its salts—molybdates. Industrially, two principal processes are employed for the production of anhydrous molybdic oxide. One of them is based on the volatility of MoO_3 and consists in directly driving off the anhydride. The other calls for the leaching of MoO_3 from the roasted concentrate with ammonia solutions with the formation of water-soluble ammonium molybdate, $(\text{NH}_4)_2\text{MoO}_4$. Irrespective of the way a concentrate is treated, the first step in the production of molybdenum is roasting in order to convert MoS_2 into MoO_3 .

Roasting of Molybdenum Concentrates. The basic reaction of roasting is the oxidation of molybdenite:



The sulphides of copper, iron and other metals are oxidised similarly to form respective oxides and sulphurous gas.

The roasting temperature should not exceed 650°C , or the MoO_3 may be melted due to local overheating and high volatility.

The vapour pressure of molybdic oxide varies with temperature as follows:

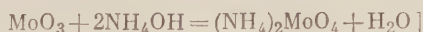
Deg. C	650	800	900	1000	1100	1150
P, mm Hg	0.05	10.1	53.9	198.3	476.2	760.0

Because of the low roasting temperature, the calcine carries much sulphur as sulphates of iron, copper, zinc, lead, and calcium. Being an acidic oxide, molybdic anhydride reacts in roasting with oxides of copper, iron, lead and calcium to form molybdates, notably CuMoO_4 , FeMoO_4 , CaMoO_4 , PbMoO_4 , etc.

In most cases molybdenum concentrates are roasted in multi-hearth roasting furnaces. They differ from those described in Chapter VI only in the manner of gas discharge. As a precaution against local overheating and as a means to control the hearth temperatures, each hearth of the roaster is equipped with an individual gas outlet connected to a common header flue. With good dust-catching equipment, a somewhat increased dust carry-over is not a problem, since the dust can be returned to the process.

Molybdenum concentrates are also roasted in rotary kilns lined with firebrick, and fluidised-bed furnaces.

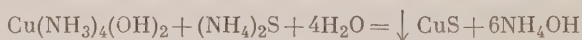
Breakdown of Roasted Concentrates with Ammonia. The principal reaction is:



Also passing into solution are the impurities copper and zinc whose sulphates and oxides form water-soluble complex ammonium salts, while ferrous iron forms a hydrosol. The silica and other components of the gangue are left in the residue. The content of impurities in the resulting liquor may be reduced by washing the roasted concentrate with water prior to leaching.

The operation is carried out in hermetically sealed horizontal iron drums or in tanks equipped with mechanical stirrers. Usually the concentrate is treated with a fresh 8- or 9-per cent solution of ammonia twice. Sometimes, the tailings of the first leach are reroasted prior to the second leach. After the second leach the tailings still carry 5 to 10 per cent Mo which is recovered by the alkali-hydroxide or soda process. The incomplete recovery of molybdenum by the ammonia process is due to the formation of molybdate during the roasting or the incomplete oxidation of the MoS_2 . The MoO_3 content of the ammonia liquor may be as high as 140 to 190 grams per litre.

The ammonia liquor is then purified in order to eliminate its copper and iron contents. The two impurities are precipitated as sulphides by ammonium sulphide:



The excess of ammonium sulphide reacts with the ammonium molybdate to form a thiosalt, and the liquor is contaminated with sulphur:



To break up the $(\text{NH}_4)_2\text{MoS}_4$, lead nitrate is added to the solution:



There must be a very slight excess of lead sulphide, for it fixes some molybdenum into insoluble lead molybdate.

The precipitated sulphides are filtered off, and the clear liquor is treated to precipitate molybdic acid or ammonium paramolybdate.

Molybdic acid is precipitated according to the reaction



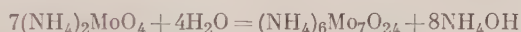
It is not advisable to run the ammonium molybdate solution into hydrochloric acid, because this produces fine crystals difficult to filter off and wash. A better method is to gradually add hydrochloric acid to the molybdate solution until pH 3.5-4 is reached. The precipitate thus thrown down consists of polymolybdate of variable compo-

sition, notably $(\text{NH}_4)_2\text{MoO}_4\text{O}_{13}$. After about 95 per cent of the total molybdenum has been precipitated, the remainder is brought down separately by adding more HCl to pH 2-2.5 as H_2MoO_4 which is returned to the process.

The solubility of H_2MoO_4 is 4.21 g/litre at 18°C , and so the precipitation cannot be complete. The remainder is precipitated from the filtrate with calcium chloride as calcium molybdate, CaMoO_4 .

Pure molybdic acid is obtained by dissolving the precipitated polymolybdate in ammonia and the solution is reprecipitated. The reprecipitate carries about 0.1 per cent impurities.

As often as not molybdenum is precipitated from ammonia solutions as ammonium paramolybdate which is a product of incomplete hydrolysis:



The solution is evaporated at 80°C to specific gravity 1.38-1.4 by driving off some ammonia, the thickened solution is cooled, and large crystals of ammonium paramolybdate separate out. The mother liquor is again evaporated, and another batch of crystals is obtained. A total of five crystallisations is carried out.

The final mother liquor is treated to precipitate the remaining molybdenum as calcium or iron molybdates which are treated separately.

Precipitated molybdic acid or ammonium paramolybdate is then calcined at 400-450 C in muffle or other furnaces to molybdic oxide.

Fig. 247 shows a flow-sheet for the breakdown of molybdenum concentrates by the ammonia process.

Breakdown of Molybdenum Concentrates by Distillation. By this process molybdic oxide is driven off from the roasted concentrate at $900\text{-}1100^\circ\text{C}$.

The yield of molybdenum trioxide from concentrates carrying considerable amounts of the calcium, iron and copper impurities is reduced due to the formation of oxides by these impurities during the roasting operation. Lead molybdate is volatile; should there be any lead in the concentrate, it will contaminate the distilled product.

A distillation furnace (Fig. 248) is an inclined rotary crucible of quartz. The temperature inside the crucible is held at $900\text{-}1100^\circ\text{C}$ by an electrical heating element. The molybdic anhydride in the furnace is kept in molten form. Air is continuously drawn over the heated surface and sweeps the MoO_3 vapour through a port in the furnace into a metal flue leading to a bag filter where the pure MoO_3 is collected.

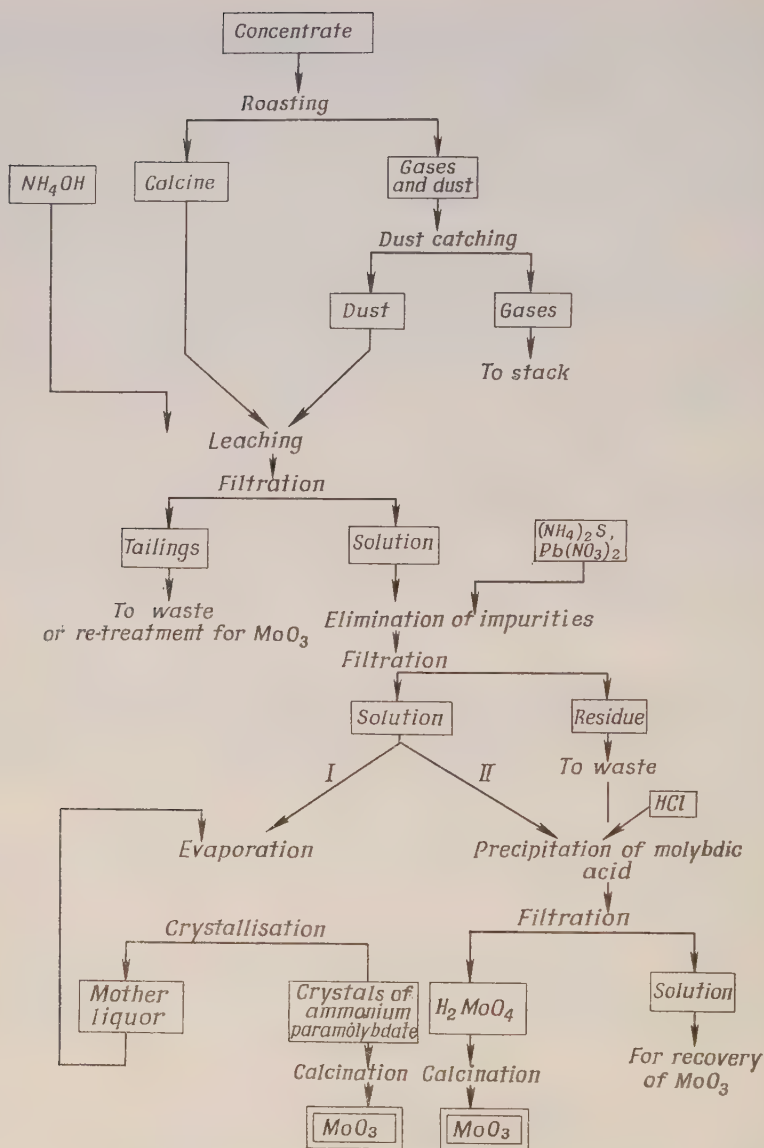


Fig. 247. Flow-sheet for treatment of molybdenum concentrates by the ammonia process

If the original concentrate is sufficiently pure, the distilled product may be 99.95 per cent pure.

The distillation process is simpler than the ammonia process, but it is only applicable to very rich and pure concentrates. The

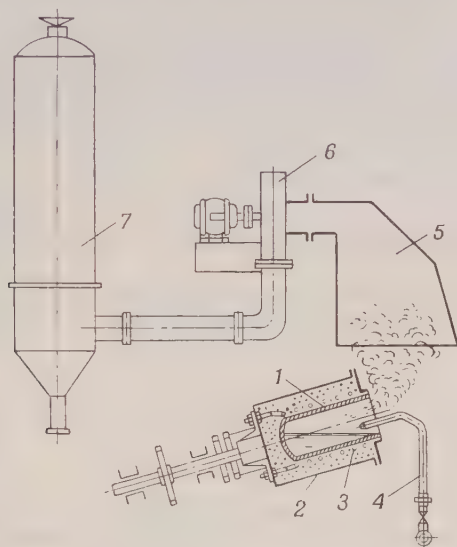


Fig. 248. Distillation furnace for molybdenic oxide:

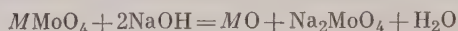
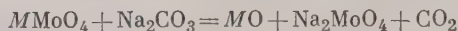
1—quartz crucible; 2—shell; 3—electric heater; 4—air in; 5—exhaust hood; 6—fan; 7—bag filter

tailings still contain about one-fifth of the original molybdenum and require re-treatment.

Breakdown of Molybdenum Concentrates with Caustic Soda and Sodium Carbonate. These two processes are applicable to low-grade molybdenum concentrates in which some molybdenum is present in the form of molybdates of iron, calcium, lead and other metals. This grade of material is obtained from the dressing of copper-molybdenum ores or comes as the tailings of the ammonia distillation processes. The molybdenum content is usually 5 to 20 per cent.

The concentrates or tailings are first roasted to oxidise their MoS_2 content and then treated with either caustic soda or sodium carbonate. In some cases the treatment requires concentrated solutions of these reagents and concurrent heating. In other cases, the raw material has to be fused with sodium carbonate or NaOH and then leached with water.

Irrespective of the actual procedure, the following reactions take place:

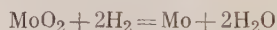
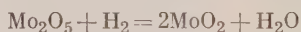


The symbol "*M*" stands for Cu, Ca, Fe or Pb.

After filtration, the sodium molybdate liquor is treated to precipitate the calcium or iron molybdate. These compounds are suitable for the direct production of ferro-molybdenum, while calcium molybdate may be used as an alloying addition in the manufacture of molybdenum steels in electric furnaces.

148. Molybdenum Metal Powder and Ductile Molybdenum

The reduction of molybdenum trioxide to molybdenum metal involves three steps corresponding to the three oxides of molybdenum:



The first reaction is easier to carry out than in the case of tungsten, while the last requires more elevated temperature and lower water vapour contents in the gases. The partially reduced MoO_3 may melt at 500-600°C; to avoid this the first step is carried out at 450°C, and the second at 1100°C.

Molybdenum metal powder is pressed into bars under a pressure of 3000 kg/sq cm. The pressed bars are then treated much as tungsten bars are. Presintering, or baking, is carried out at about 1200°C, and the final, or high-temperature, sintering at 2200-2400°C.

Sintered bars are swaged and drawn at temperatures 100-300°C lower than for tungsten.

Large ingots and blanks of molybdenum are produced by melting it in vacuum arc furnaces. An arc is struck between an electrode made up of sintered molybdenum bars and a pool of molten metal held in a water-cooled copper mould. Water cooling prevents the copper from alloying with and contaminating the molybdenum. A sketch of such a furnace is shown in Fig. 249.

A more recent addition to the manufacture of molybdenum is electron-beam melting. By this method, molten molybdenum can be held in a deep vacuum for a long time and get rid of many volatile impurities. The principle of electron-beam melting will be readily understood from reference to Fig. 250. A beam of electrons is ejected by a hot tungsten or tantalum cathode held at a very high negative

potential. Passing through an opening in an earthed anode 2, the electron beam is focused by an electromagnetic coil 3, much as a beam of light is focused by lenses, and is directed onto the tip of

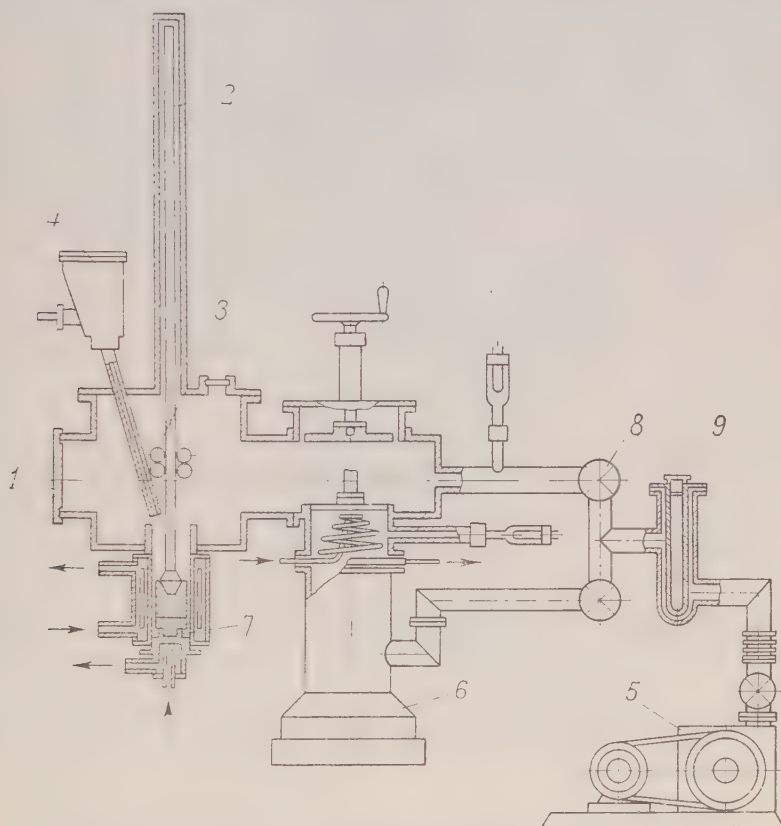


Fig. 249. Diagram of a vacuum arc furnace for the melting of molybdenum with a consumable electrode:

1—vacuum chamber; 2—consumable molybdenum electrode; 3—feed rollers; 4—feeder for alloying additions; 5—fore-vacuum pump; 6—steam-jet pump; 7—water-cooled copper mould; 8—vacuum cocks; 9—liquid nitrogen-cooled trap

a blank consisting of pressed molybdenum bars. As the electrons strike at the blank, their tremendous kinetic energy is converted to heat, the blank grows hot and finally melts.

The electron gun, which supplies and focuses electrons, operates in a high vacuum of the order of 10^{-4} to 10^{-5} mm Hg. The best utilisation

tion of energy is obtained at a voltage of 30 to 35 kilovolts, because the accompanying X-rays account for a negligible share of overall

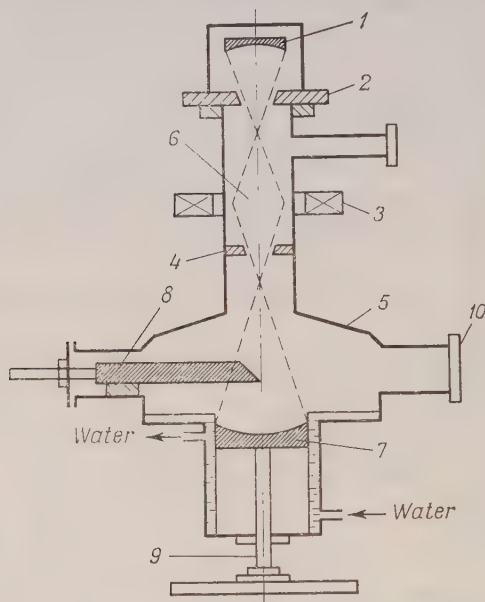


Fig. 250. Diagram of electron-beam furnace:

1—electron-gun cathode; 2—anode; 3—electromagnetic coil; 4—diaphragm; 5—melting chamber; 6—electron beam; 7—water-cooled copper mould; 8—sintered bars; 9—ingot-pulling device; 10—vacuum connection

radiation, and the efficiency of the plant is 95 per cent. Large ingots of molybdenum can be produced by gradually lowering the bottom of the mould.

149. Recovery of Other Values from Molybdenum Ores

The copper content of copper-molybdenum ores is recovered by selective flotation. The copper and molybdenum concentrates thus obtained are treated as already described.

The rhenium content is recovered as follows. In roasting, the rhenium sulphide, which is isomorphic with molybdenum, is oxidised and volatilises as Re_2O_7 . Its content in the roasting dust may be as high as 0.2 per cent.

The dust is lixiviated with water, and the resulting liquor is digested; rhenium is present in the liquor as rhenic acid, HReO_4 . An addition of a potassium salt throws down a poorly soluble potassium perrhenate, KReO_4 .

Chapter XXI

THE METALLURGY OF TITANIUM

150. General

Titanium is a silvery metal with a specific gravity of 4.51. Alpha-titanium has a hexagonal structure while the lattice of beta-titanium is body-centred cubic. The metal melts at 1660°C and boils at 3400°C.

The mechanical properties of titanium depend to a great degree on its purity. Dissolved gases (oxygen, nitrogen or hydrogen) make it brittle, while pure titanium metal is malleable. Pure titanium metal has a hardness of 73 on the Brinell scale, while commercial titanium shows a hardness of 180-280. The tensile strength varies within a narrower range: from 27 to 64 kg/sq mm, respectively. If compacted prior to fabrication, commercially pure titanium has a Brinell hardness of about 280 and a tensile strength of 77-86.

Titanium forms compounds in valences of 4 to 2, the tetravalent one is most common, ions Ti^{2+} and Ti^{3+} being strong reducers.

Titanium is attacked slowly by concentrated nitric and diluted sulphuric acids while it is attacked rapidly by concentrated HCl , H_2SO_4 , HF and aqua regia. It resembles Cr-Ni stainless steels in resistance to corrosion. In air, titanium is very stable and up to about 500°C does not change much its mechanical properties. When heated above that point, it eagerly absorbs oxygen to become embrittled. Heated to 800°C, titanium readily absorbs nitrogen to form with it solid solutions and a nitride, TiN , possessing high hardness. The absorption of hydrogen by titanium is related to the formation of hydrides TiH and TiH_2 .

The lowest oxide, TiO , is a base, while the highest oxide, TiO_2 , is amphoteric.

The commercial interest in titanium metal as a structural material and a basis for alloy manufacture arose recently after methods had been devised for its production in sufficiently pure form. Prior to that, titanium had been considered very brittle and unsuitable for forming.

The value of titanium as a structural metal, especially for aircraft, lies in the happy combination of high mechanical strength, resistance to corrosion and heat, and light weight. Alloying it with manganese, chromium, aluminium, vanadium, molybdenum, silicon, boron and carbon appreciably improves the mechanical and anticorrosive properties of titanium metal.

Titanium and its alloys have a density of about 4.5-5 g/cu cm. In strength, they are superior to many alloy steels and aluminium-magnesium light-weight alloys, especially at 200-400°C. This is why titanium alloys are successfully used in the manufacture of fuselages and engines for jet planes, components for marine propulsion plant, and internal-combustion engines. The high resistance of these alloys to corrosion is utilised in chemical engineering. Titanium carbide TiC is extremely hard and refractory. Along with tungsten carbide, it is used in the fabrication of cermets.

The wide use of titanium metal is handicapped by its high cost, existing methods of titanium metal production being difficult, slow and expensive. Yet, as costs are reduced by improvements in production methods, consumption should rise rapidly.

As an alloying addition to steels and non-ferrous alloys titanium has been used for a long time already. The high affinity of titanium for oxygen, nitrogen, sulphur and carbon has a far-reaching cleansing effect on intercrystalline inclusions and dissolved gases in the base steel.

Titanium dioxide, TiO_2 , which is a finely divided white powder, is the most commonly used of all titanium products. As a result of its extreme whiteness, brightness and high index of refraction, titanium dioxide is widely used as a white pigment in paints and enamels. In 1958 world output of TiO_2 was 800,000 tons.

151. Sources of Titanium

Of all the many titanium minerals the most important are rutile TiO_2 and ilmenite $xFeTiO_3 \cdot yFe_2O_3$. Rutile is the most stable naturally occurring modification of titanium dioxide. Its other modifications, brookite and anatase, occur seldom. Natural rutile contains as much as 10 per cent oxides of iron and other metals, which impart it brown, red or bluish colour. In nature, ilmenite occurs in placers mixed with magnetite (Fe_3O_4) and hematite (Fe_2O_3). Laths of ilmenite in a matrix of magnetite form titanomagnetite ores. In this ore the titanium content may be as high as 20 per cent. Titanomagnetites differ in the size of ilmenite laths and in their relation to iron minerals. Coarse-grained ilmenite (with particles 0.1-0.2 mm across) can be easily separated from the magnetite matrix by magnetic separation. Fine-grained ilmenite which sometimes forms solid solutions of the type TiO_2 - Fe_3O_4 is difficult to separate by this method. Silicates and other relatively light-weight impurities can be separated from ilmenite by tabling. The specific gravity of ilmenite is 4.56-5.21. A typical ilmenite concentrate will have the following composition (in per cent): TiO_2 , 42; FeO , 28; Fe_2O_3 , 21; CaO , 1.0; SiO_2 , 2.0; Al_2O_3 , 2.5; MgO , 2.5.

Rutile concentrates may carry up to 95 per cent TiO_2 . However, rutile ores are relatively rare, being concentrated in Americas and Australia. These ores alone cannot provide for the rapid expansion of titanium metallurgy expected in the foreseeable future.

On the other hand, the minerals perovskite, CaTiO_3 , and sphene, $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$, often occur in big deposits. The former is an associate of ilmenite, rare-earth minerals and tantalum-niobates; the latter is found in apatite, nepheline and some other rocks. Both minerals are easy to separate by gravity concentration and flotation, but their treatment is yet in the developmental stage because of the difficulties in the recovery of their tantalum, niobium and rare-earth contents.

152. Treatment of Ilmenite Concentrates

The type of treatment given to ilmenite concentrates depends on the final product sought for. For the production of titanium metal, this will be titanium tetrachloride, TiCl_4 , prepared by the combined reduction and chlorination of ilmenite. Titanium dioxide, on the other hand, may be the final product where white pigment is required. True, in some, fairly rare cases titanium dioxide may be reduced to titanium metal, but existing methods are still very cumbersome and expensive.

In the manufacture of ferro-titanium, which is used as a steel deoxidiser and alloying addition, ilmenite is subjected to reduction smelting directly to obtain an alloy which contains 18 per cent Ti, 5-8 per cent Al, 3.5-6 per cent Si, 3-4 per cent Cu and up to 1 per cent of the impurities S and P. Ilmenite concentrates may also be subjected to reduction smelting in electric furnaces to give titanium-bearing irons and slag with 70 to 80 per cent TiO_2 which serves as the source material for the production of titanium tetrachloride.

153. The Production of Titanium Tetrachloride

Titanium tetrachloride may be obtained by the chlorination of a mixture of titanium dioxide and carbon at 600-800°C, according to the equations:



The first two reactions are particularly rapid. Titanium tetrachloride is obtained in vapour form as it boils at 136°C.

Commercial practice does not use ilmenite for the preparation of titanium tetrachloride by this method owing to the formation of large quantities of FeCl_3 which is also volatile (boiling point, 319°C) which calls for the separate condensation of TiCl_4 and FeCl_3 —a task difficult to accomplish.

The usual practice is to chlorinate the slag obtained from the reduction smelting of ilmenite and containing 80-87 per cent TiO_2 , or rutile concentrate.

Slags carrying so much titanium dioxide are very viscous. If they are to be fluid while molten, the temperature should be over 1500°C , a figure hardly obtainable in the hearth of a blast furnace. This is why use is made of arc furnaces with as little flux added as possible. The resultant slag contains up to 87 per cent TiO_2 . The furnaces used for the purpose are usually three-arc types with a power rating of up to 10,000 kVA.

The charge is made up of ilmenite concentrate, coke or anthracite with a grain size of about 4 mm. As much of the reducing agent is added as is necessary to obtain a slag containing about 5 per cent FeO . In order to keep down energy consumption, one half of the charge is briquetted, and the other half is charged as a powder. The recovery of titanium into the slag exceed 90 per cent. An approximate composition of the slag is TiO_2 , 86 per cent; FeO , 6 per cent; SiO_2 , 5 per cent; Al_2O_3 , 2 per cent; $\text{CaO} + \text{MgO}$, 4 per cent.

In either case, the material is mixed and ground with coke and the mixture bound with coal tar. This mixture is briquetted and the briquettes are heated in a kiln at 800°C in the absence of air. The resulting hard and porous mass is fed into a chlorinator.

A chlorinator is an electric shaft furnace such as described in the chapter on the chlorination of caustic magnesium (Fig. 222).

Figure 251 shows a diagram of a plant for the condensation of TiCl_4 . The dust carried away from the furnace by the flue gas is caught by an air-cooled dust chamber where the bulk of the chlorides of iron and aluminium is also condensed; the temperature of the gas leaving the chamber is $160\text{--}180^\circ\text{C}$. The gas then enters a checker-work-packed tower sprinkled with cooled liquid TiCl_4 . The bulk of the titanium tetrachloride is removed from the gas into the liquid which catches the remaining dust and solid chlorides and carries them into a collector, and from the collector into a thickener. Some of the liquid taken from the collector is cooled and directed to cool the tower.

For further removal of TiCl_4 , the gas leaving the cooling tower is passed through a tubular cooler with a temperature of minus $10\text{--}15^\circ\text{C}$ and then through a scrubber sprinkled with lime milk. This prevents the contamination of the atmosphere with chlorine or hydrogen chloride. The titanium tetrachloride thus obtained

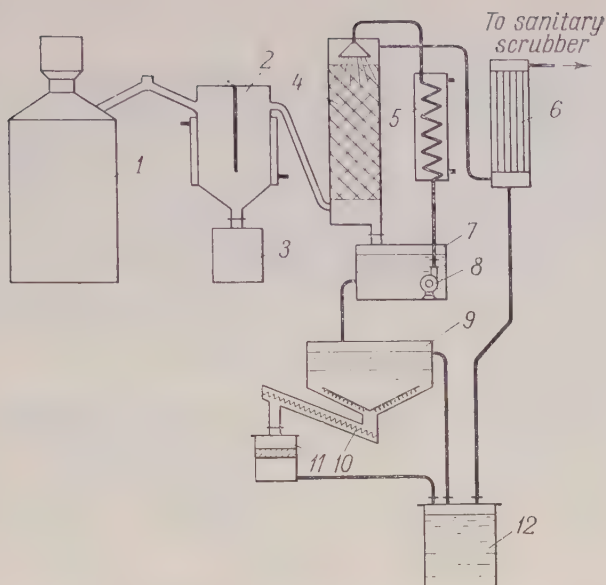


Fig. 251. Diagram of plant for the condensation of titanium tetrachloride:
 1—shaft furnace for chlorination; 2—dust chamber and condenser for solid chlorides
 3—dust and condensate collector; 4—tower sprinkled with TiCl_4 ; 5—cooler for liquid
 TiCl_4 ; 6—tubular condenser; 7— TiCl_4 collector; 8—pump; 9—thickener; 10—slime-
 discharging auger; 11—filter; 12—collector for technical TiCl_4 .

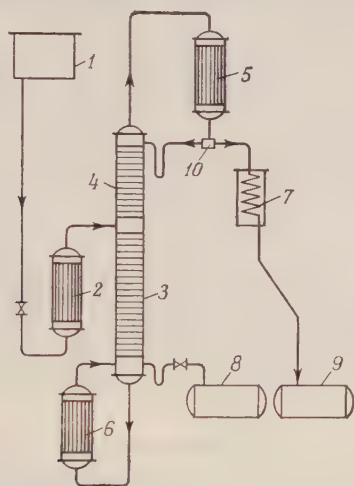


Fig. 252. Diagram of continuous purification:
 1—pressure tank; 2—heater; 3—discharge portion of column; 4—supporting portion
 of column; 5—deflector; 6—still; 7—cooler for distillate; 8—collector for still residue;
 9—distillate collector

is finally filtered through a porous ceramic mass or activated charcoal, after which it has the following analysis: TiCl_4 , 97-99 per cent; SiCl_4 , 1.5-2.5 per cent; FeCl_3 (after filtration), 0.02-0.002 per cent; Cl_2 , 0.1-0.03 per cent; and V up to 0.2 per cent.

The recovery of titanium into this product is about 90 per cent.

The impurity vanadium oxychloride boils at about the same temperature and it is therefore difficult to separate it by fractional distillation. This is why, prior to fractional distillation, VOCl_3 is reduced with powdered copper to compounds boiling at a higher temperature, namely COCl_2 , VO_2 , etc. The treatment with powdered copper also reduces other low-boiling-point compounds, such as SnCl_4 and CrO_2Cl_2 .

Fractional distillation is based on a principle similar to one used in the removal of lead and cadmium from zinc. Fractional distillation is carried out in stills with stainless trays having either round openings or slots. The highest rate of distillation has been attained by a continuous process diagrammatically shown in Fig. 252. Pure titanium tetrachloride is a clear or yellowish liquid, totalling not over 10^{-3} to 10^{-4} per cent impurities.

The recovery of TiCl_4 from the technical product is about 95 per cent.

The titanium tetrachloride thus filtered and purified is then subjected to fractional distillation to separate off most of the volatile chlorides and oxychlorides, utilising their difference in boiling points. The boiling points of some of them are compared below:

Compound	TiCl_4	FeCl_3	VCl_4	VOCl_3	SiCl_4
Deg. C	136	319	164	127	57

The fractional distillation is carried out in two stages, the first to be distilled off being the SiCl_4 while in the second still the TiCl_4 is driven off to condense in the condenser as a transparent colourless liquid (it melts at -23°C).

154. The Production of Titanium Metal

Commercially, titanium tetrachloride is reduced by magnesium (the Kroll process). The reaction is exothermic and may be therefore carried out at $800\text{-}900^\circ\text{C}$:



This is an intermittent process using hermetically sealed stainless retorts filled with an inert gas argon or helium. The retorts are placed in an upright position in an electric-heated or a gas-fired furnace. From above each retort is closed with a lid having a rubber

seal cooled by a local water cooler. The lid has ports for charging magnesium ingots, feeding of TiCl_4 , evacuation of air, and supply of the inert gas. Each retort is large enough to yield as much as 1500 kg of titanium sponge (as the product is termed) in a single run.

After a retort has been placed in a furnace, evacuated and filled with the inert gas, molten magnesium is poured at a temperature of about 700°C and liquid titanium tetrachloride is fed in. The heater element is turned off, and the temperature is maintained anywhere between 800 and 900°C by varying the rate of feed of TiCl_4 . Sometimes, the retort may be blown with air from the outside. Abstraction of excess heat speeds up the reduction. Liquid magnesium chloride is run off through a port in the bottom of the retort at regular intervals. After the requisite quantity of TiCl_4 has been fed in and the reaction has stopped of its own accord, the heater is turned on, and retort is allowed to stay at 900°C for about an hour so that the reduction may reach completion. Next, the retort is removed from the furnace by crane and cooled with water. Now the retort contains titanium sponge, the residual magnesium chloride filling the pores in the sponge, and excess magnesium.

The products of the reaction are separated in a vacuum at a temperature of 900°C , utilising the difference in vapour pressure between them. Under such conditions, the pressure of titanium vapours is negligible, while for magnesium chloride it is about 8 mm, and for magnesium metal, about 80 mm Hg.

The lid is lifted off the retort, and a condenser is set up instead. The retort is again loaded and sealed inside the furnace so that a vacuum can be obtained both inside and outside the retort (Fig. 253). This is done in order to protect the walls of the retort from deformation by atmospheric pressure. Since there is a vacuum both inside and outside the retort, the pressure difference is nil, and the hot walls of the retort are relieved of any load.

The magnesium and magnesium chloride are distilled off at a temperature of 900°C and a vacuum of about 10^{-4} mm Hg during 25 hours. Next the retort is allowed to cool, and the titanium sponge is knocked out of it with air-operated chisels. The composition of the sponge is: H_2 , 0.002 per cent; O, 0.05 per cent; N_2 , 0.02 per cent; Cl, 0.07 per cent; Mg, 0.08 per cent; and C, 0.1 per cent.

At some plants, the distillation of magnesium and magnesium chloride is carried out in other retorts into which the products of the reduction stage are loaded in a specially dry location where atmospheric moisture cannot bring about the partial hydrolysis of MgCl_2 with the formation of oxychlorides, such as MgOHCl , difficult to distill off. By this method, the capacity of the retorts is utilised more fully, but the dry atmosphere is a grave handicap to operators.

Alternatively, titanium tetrachloride can be reduced by sodium which is cheaper than magnesium. The titanium sponge, however, is more difficult to separate from NaCl than from MgCl_2 by vacuum

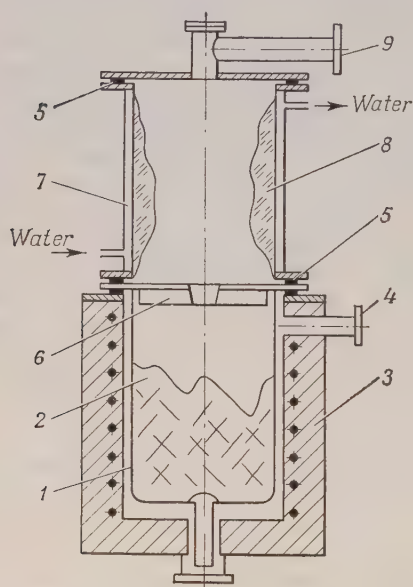


Fig. 253. Plant for separation of titanium sponge from residual MgCl_2 and excess magnesium:

1—retort; 2—products of reaction; 3—sealed electric furnace; 4—furnace evacuation port; 5—rubber seals; 6—screens; 7—condenser; 8—Mg and MgCl_2 condensate; 9—port for removal of gases from retort

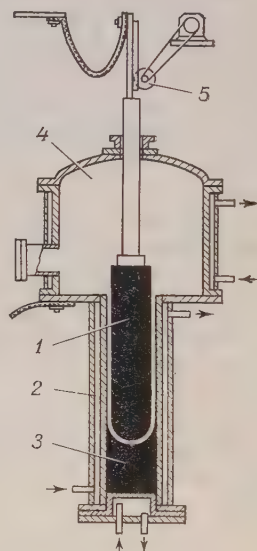
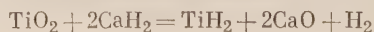


Fig. 254. Diagram of an arc furnace using a consumable electrode for the melting of titanium:

1—consumable electrodes made from titanium sponge; 2—water-cooled copper mould; 3—titanium ingot; 4—vacuum chamber; 5—electrode-handling mechanism

distillation because the volatility of NaCl is negligible. The leaching of the reacted mass is disadvantageous, for it involves the surface oxidation of the sponge.

Still another reduction process is based on the use of titanium dioxide and metallic calcium or calcium hydride as the reducing material. Prior to use, the calcium is purified by distillation. The reactions may be expressed by the following equations:



The calcium process, however, requires higher temperatures of the order of 1000-1100°C and a large excess of reducing material (25 to 50 per cent). Furthermore, the titanium sponge obtained by this process is more contaminated by oxygen and contains 99-99.5 per cent Ti.

After purification the sponge may be ground to powder and pressed into shape or melted in a special electric furnace and cast into ingots.

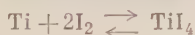
The pressing is done in steel moulds under a pressure of 7 or 8 tons sq cm, and the bars are sintered in a vacuum (10^{-4} mm Hg) at 1000-1100°C for 15 or 16 hours. The powder-metallurgy process, however, suffers from low production rates and the difficulty of obtaining large sintered bars.

The electric-arc melting of the sponge in a water-cooled crucible and in a vacuum is much more attractive on many counts.

The consumable electrode for arc-melting is made of titanium sponge reduced to particles measuring 5 to 30 mm in diameter, pressed in steel moulds under a pressure of 2-4 tons/sq cm. The cylinders thus obtained with a diameter of up to 50 cm are welded by the argon-arc process into a single bar. Alternatively, the pressings may be joined together in the furnace by passing a current through them while a pressure of about 1 ton/sq cm is applied.

The arc furnace operates under a vacuum of about 0.01 mm Hg, using direct current (Fig. 254). With a current of 9000 amperes and a voltage of 30 volts, the rate of melting is about 4.4 kg/min, and energy consumption is 4.8 kWh/kg of titanium. This method produces ingots weighing up to 4 tons.

A very pure metal (99.9-99.95 per cent Ti) can be obtained from the sponge by the iodide process which is based on the following reaction: a volatile titanium iodide is formed by direct action of the iodine on the impure titanium metal at a low temperature in the presence of a filament which is heated electrically to a temperature above that at which the iodide will decompose. Coming in contact with the hot filament, the titanium iodide will, therefore, dissociate, the metal being deposited on the filament surface. This process may be presented in equation form as follows:



At 100-200°C this reaction proceeds to the right and at 1300-1500°C to the left.

A diagrammatical drawing of an apparatus for the iodide process is shown in Fig. 255. The sponge is charged into the annular space between the reactor wall and a perforated molybdenum cylinder. Inside the reactor is placed a tungsten filament electrically heated to 1300-1500°C while the reactor is heated to 100-200°C in a ther-

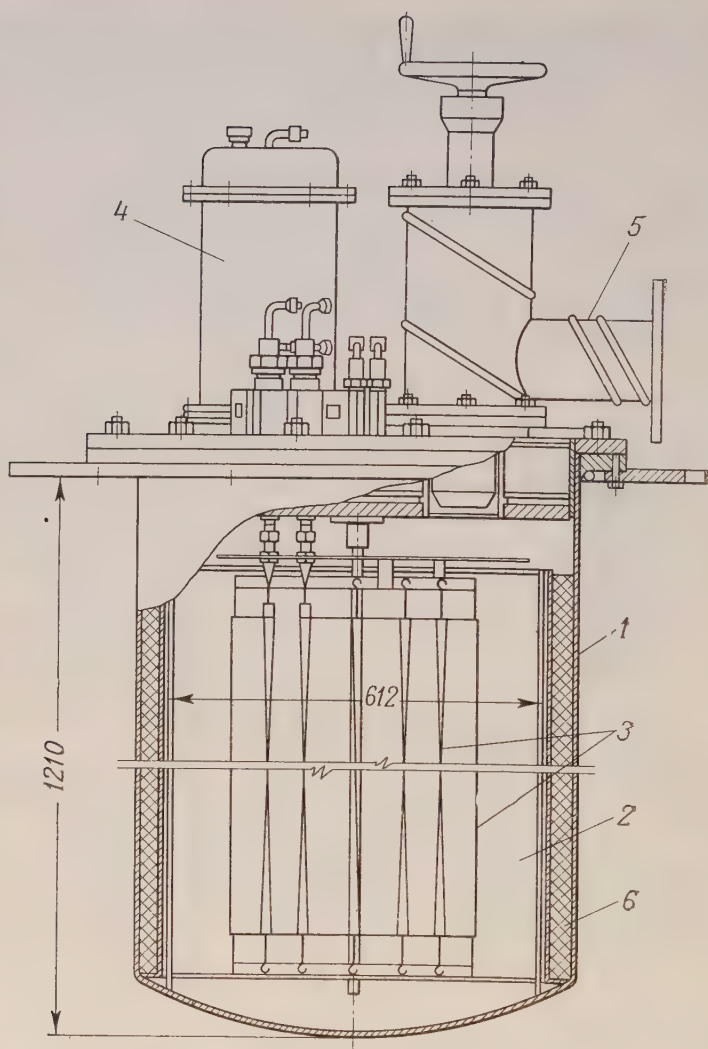


Fig. 255. Apparatus for the iodide process of titanium production:
 1—housing; 2—perforated molybdenum retainer; 3—titanium filaments; 4—chamber
 or iodine bulb; 5—port for connection of vacuum pump; 6—titanium sponge

mostated oven. After the reactor has been charged, a vacuum is built up in it of the order of 10^{-1} mm Hg, and a bulb of iodine is broken within it. The iodine vapours enter into the above reaction to form vapours of TiI_4 from the sponge, and the remainder of the process proceeds as described. The deposited metal is built up in a compact form, and the filament gradually becomes a rod of considerable thickness.

The iodide process cannot, however, be considered a true commercial process, since its production rate is about 10 kg per day and the metal produced is very expensive.

APPENDIX I

Standard Free Energies of Reaction of Selected Compounds

$$\Delta G_T = A + BT \log T + CT$$

Reaction	ΔG in cal.			Temp. range, °K	\pm kcal
	A	B	C		
$[Al] + 1^{1/2}\langle Cl_2 \rangle = \langle AlCl_3 \rangle$	-140400	2.5	7.05	> 933	8
$2Al + 1^{1/2}\langle O_2 \rangle = Al_2O_3$	-400810	-3.98	87.64	298-923	3
$2[Al] + 1^{1/2}\langle O_2 \rangle = Al_2O_3$	-405760	-3.75	92.22	923-1800	4
$C + 1^{1/2}\langle O_2 \rangle = \langle CO \rangle$	-26700	—	-20.95	298-2500	1
$C + \langle O_2 \rangle = \langle CO_2 \rangle$	-94200	—	-0.2	298-2000	1
$2Ca + \langle O_2 \rangle = 2CaO$	-302650	—	47.32	298-1124	3
$2[Ca] + \langle O_2 \rangle = 2CaO$	-307100	—	51.28	1124-1760	1.5
$2Ca_{\alpha} + \langle S_2 \rangle = 2CaS$	-258870	—	45.62	298-673	2
$2Ca_{\beta} + \langle S_2 \rangle = 2CaS$	-259100	—	45.92	673-1124	2
$CaO + \langle CO_2 \rangle = CaCO_3$	-40250	—	34.4	298-1150	1
$CaO + SiO_2 = CaSiO_{3\alpha}$	-21300	—	0.12	298-1483	1
$CaO + SiO_2 = CaSiO_{3\beta}$	-19900	—	-0.82	1483-1813	2
$2CaO + SiO_2 = Ca_2SiO_4$	-30200	—	-1.2	298-1700	2.5
$2Co + \langle O_2 \rangle = 2CoO$	-111800	—	33.8	298-1400	2
$3CoO + 1^{1/2}\langle O_2 \rangle = Co_3O_4$	-43800	—	35.4	298-1300	3
$2Cu + 1^{1/2}\langle O_2 \rangle = Cu_2O$	-40500	-3.92	29.5	298-1356	1
$Cu_2O + 1^{1/2}\langle O_2 \rangle = 2CuO$	-34950	-6.1	44.3	298-1300	0.5
$2Cu + 1^{1/2}\langle S_2 \rangle = Cu_2S_{\gamma}$	-34150	-6.22	28.74	623-1360	1
$Fe + 1^{1/2}\langle O_2 \rangle = FeO$	-62050	—	14.95	298-1642	3
$[Fe] + 1^{1/2}\langle O_2 \rangle = [FeO]$	-55620	—	10.83	1808-2000	3

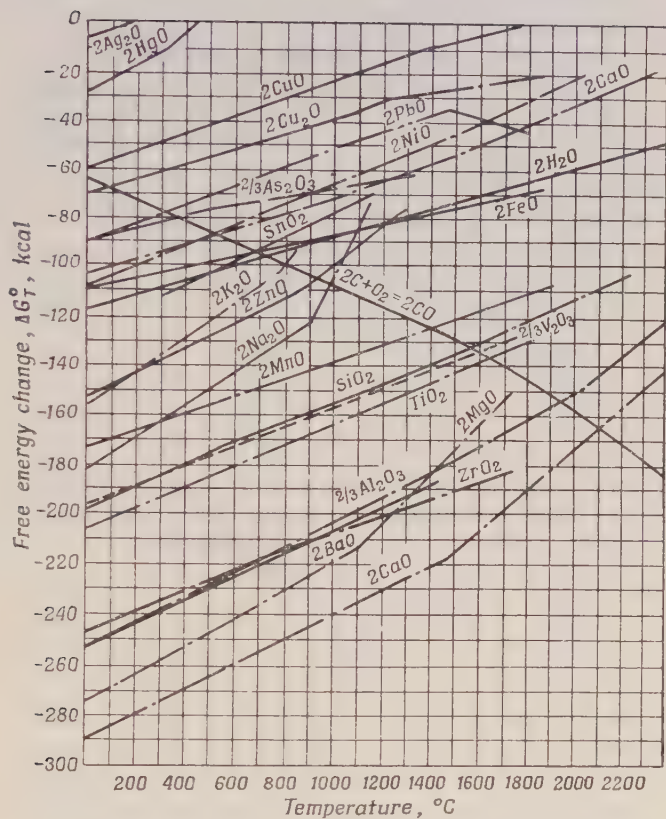
Brackets around symbols denoting molar quantities: < > gaseous; [] liquid; no brackets, solid.

(cont'd)

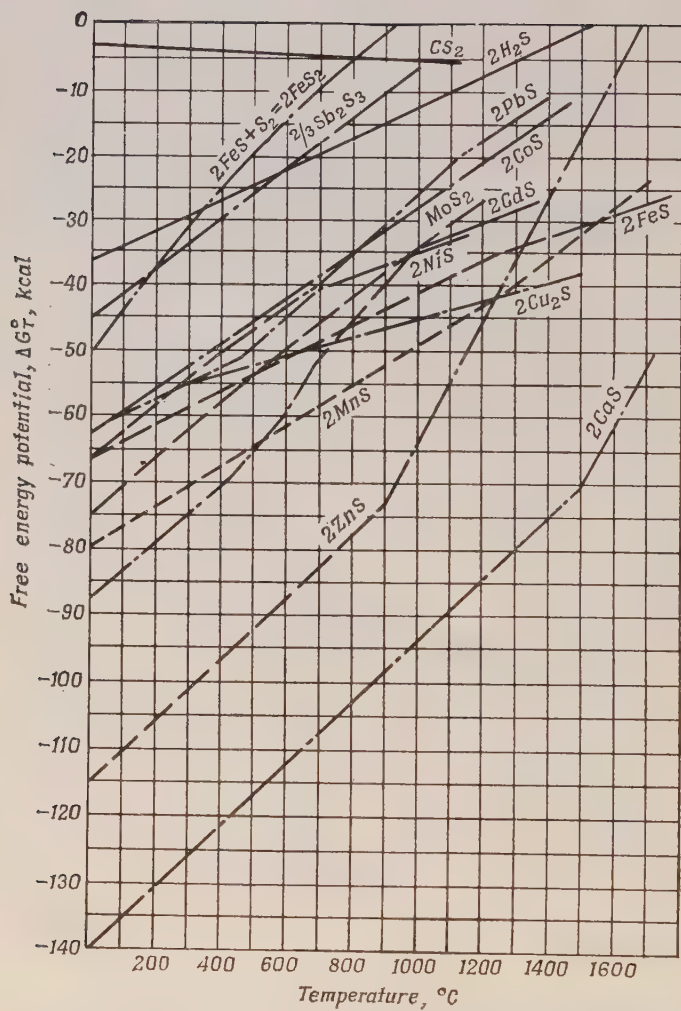
Reaction	ΔG in cal.			Temp. range, °K	± kcal
	A	B	C		
$3\text{FeO} + \frac{1}{2}\langle\text{O}_2\rangle = \text{Fe}_3\text{O}_4$	-74620	—	29.9	298-1642	3
$2\text{Fe}_3\text{O}_4 + \frac{1}{2}\langle\text{O}_2\rangle = 3\text{Fe}_2\text{O}_3$	-59620	—	33.62	298-1460	8
$2\text{Fe}_\alpha + \langle\text{S}_2\rangle = 2\text{FeS}_\beta$	-71820	—	25.12	412-1179	1
$2\text{Fe}_\gamma + \langle\text{S}_2\rangle = 2\text{FeS}_\beta$	-72140	—	25.48	1179-1261	2
$2\text{FeS} + \langle\text{S}_2\rangle = 2\text{FeS}_2$	-86700	—	90.0	600-1100	3
$2\text{Fe} + \langle\text{O}_2\rangle + \text{SiO}_2 = \text{Fe}_2\text{SiO}_4$	-135300	—	34.4	298-1478	—
$\langle\text{H}_2\rangle + \frac{1}{2}\langle\text{O}_2\rangle = [\text{H}_2\text{O}]$	-57250	4.48	-2.24	298-2500	0.3
$[\text{Mg}] + \langle\text{Cl}_2\rangle = [\text{MgCl}_2]$	-147850	-13.58	72.77	987-1376	1.5
$\text{Mg} + \frac{1}{2}\langle\text{O}_2\rangle = \text{MgO}$	-144350	-2.95	33.95	298-923	1.5
$[\text{Mg}] + \frac{1}{2}\langle\text{O}_2\rangle = \text{MgO}$	-145350	-0.24	26.95	923-1376	1.5
$\langle\text{Mg}\rangle + \frac{1}{2}\langle\text{O}_2\rangle = \text{MgO}$	-181600	-7.37	75.7	1376-2500	3
$\text{MgO} + \langle\text{CO}_2\rangle = \text{MgCO}_3$	-28100	—	40.6	298-1000	3
$\text{Mn} + \frac{1}{2}\langle\text{O}_2\rangle = \text{MnO}$	-91950	—	17.34	298-1500	3
$[\text{Mn}] + \frac{1}{2}\langle\text{O}_2\rangle = \text{MnO}$	-95400	—	19.7	1500-2050	3
$\text{Mo} + \langle\text{O}_2\rangle = \text{MoO}_2$	-140100	-4.6	55.8	298-1300	10
$\text{MoO}_2 + \frac{1}{2}\langle\text{O}_2\rangle = \text{MoO}_3$	-38700	—	19.5	298-1300	3
$\text{Ni} + \frac{1}{2}\langle\text{O}_2\rangle = \text{NiO}$	-58450	—	23.55	298-1725	2
$[\text{Ni}] + \frac{1}{2}\langle\text{O}_2\rangle = \text{NiO}$	-62650	—	25.98	1725-2200	3
$3\text{Ni} + \langle\text{S}_2\rangle = \text{Ni}_3\text{S}_2$	-79240	—	39.01	650-800	2
$2[\text{P}] + 2\frac{1}{2}\langle\text{O}\rangle = \text{P}_2\text{O}_5$	-370000	—	123.3	631-1400	30
$\text{Pb} + \langle\text{Cl}_2\rangle = \text{PbCl}_2$	-85000	—	34.3	298-771	2
$[\text{Pb}] + \langle\text{Cl}_2\rangle = [\text{PbCl}_2]$	-83600	-14.12	73.3	771-1224	3
$\text{Pb} + \frac{1}{2}\langle\text{O}_2\rangle = \text{PbO}$	-52850	-3.45	33.84	298-600	2
$[\text{Pb}] + \frac{1}{2}\langle\text{O}_2\rangle = \text{PbO}$	-54950	-8.05	50.1	600-1150	3
$\text{Pb} + \frac{1}{2}\langle\text{S}_2\rangle = \text{PbS}$	-72710	—	34.17	298-600	3

(cont'ed)

Reaction	ΔG in cal.			Temp. range, °K	± kcal
	A	B	C		
$[\text{Pb}] + \frac{1}{2}\langle\text{S}_2\rangle + 2\langle\text{O}_2\rangle = \text{PbSO}_4$	-219000	—	85.6		10
$[\text{Pb}] + \frac{1}{2}\langle\text{S}_2\rangle = \text{PbS}$	-75160	—	38.25	600-1380	3
$\langle\text{S}_2\rangle + 2\langle\text{O}_2\rangle = 2\langle\text{SO}_2\rangle$	-173240	—	34.62	298-2000	1
$\langle\text{S}_2\rangle + 3\langle\text{O}_2\rangle = 2\langle\text{SO}_3\rangle$	-218440	—	77.34	318-1800	3
$\text{Si} + 2\langle\text{Cl}_2\rangle = \langle\text{SiCl}_4\rangle$	-147300	-3.64	42.6	298-600	3
$\text{Si} + \langle\text{O}_2\rangle = \text{SiO}_2$	-210600	-3.0	52.22	298-1700	3
$[\text{Si}] + \langle\text{O}_2\rangle = [\text{SiO}_2]$	-219200	-4.15	61.37	1986-2100	5
$[\text{Si}] + \text{C} = \text{SiC}$	-24010	—	8.33	1683-2000	4
$[\text{Sn}] + \langle\text{Cl}_2\rangle = [\text{SnCl}_2]$	-79600	—	28.3	520-925	4
$\text{Ti} + 2\langle\text{Cl}_2\rangle = \langle\text{TiCl}_4\rangle$	-180700	1.8	34.65	298-1700	3
$\text{Ti} + \langle\text{O}_2\rangle = \text{TiO}_2$	-122300	—	21.3	600-2000	4
$\text{W} + \langle\text{O}_2\rangle = \text{WO}_2$	-131600	—	36.6	298-1500	5
$\text{W} + \frac{1}{2}\langle\text{O}_2\rangle = \text{WO}_3$	-201500	-10.2	91.7	298-1400	5
$\text{W} + \text{C} = \text{WC}$	-9100	—	0.4	298-2000	3
$\text{Zn} + \langle\text{Cl}_2\rangle = [\text{ZnCl}_2]$	-93950	—	27.35	586-1005	5
$[\text{Zn}] + \frac{1}{2}\langle\text{O}_2\rangle = \text{ZnO}$	-115420	-10.35	82.38	1170-2000	2
$[\text{Zn}] + \frac{1}{2}\langle\text{S}_2\rangle = \text{ZnS}$	-94970	-8.05	74.92	1120-2000	5



Standard free energies of formation of selected oxides



Standard free energies of formation of selected sulphides

APPENDIX II

Vapour Pressures of Some Volatile Substances

$$\log P = AT^{-1} + B \log T + CT + D \text{ (mm Hg)}$$

Substance	M. p.	B. p.	log P (mm Hg)				Temp. range, °K
			A	B	C · 10 ³	D	
AlF ₃	subl.	1270	-21670	-7.55	—	40.93	298-1260
Al ₂ Cl ₆	ditto	180	-6360	3.77	-6.12	9.66	298-b.p.
As	ditto	616	-6160	—	—	9.82	600-900
As ₂ O ₃	ditto	457	-3130	—	—	7.16	298-730
Cd	321	765	-5819	-1.257	—	12.287	594-1050
CdO	subl.	1497	-14590	-1.76	—	16.83	298-
CdS	decomp.	—	-11460	-2.5	—	16.06	298-1200
FeCl ₂	677	1026	-9475	-5.23	—	26.53	m.p.-b.p.
Fe ₂ Cl ₆	307	319	-10754	-12.64	—	55.9	m.p.-b.p.
Hg	-39	357	-3305	-0.795	—	10.355	298-b.p.
Mg	650	1103	-7550	-1.41	—	12.79	m.p.-b.p.
MgCl ₂	714	1418	-10840	-5.03	—	25.53	m.p.-b.p.
MoO ₃	795	1100	-12480	-4.02	—	24.60	m.p.-b.p.
Pb	327	1740	-10130	-0.985	—	11.16	m.p.-b.p.
PbCl ₂	198	954	-10000	-6.55	—	31.60	m.p.-b.p.
PbO	885	1470	-13310	-2.77	—	19.47	m.p.-b.p.
PbS	1110	1281	-13300	-0.81	-0.43	14.85	298-1200
Re ₂ O ₇	296	362	-3950	—	—	9.10	m.p.-b.p.
S	119	445	-4830	-5.0	—	23.88	m.p.-b.p.
Sb	630	1635	-11170	-3.02	—	18.54	m.p.-b.p.
Sb ₂ O ₃	656	1425	-3900	—	—	5.137	929-1073
Sb ₂ S ₃	—	—	-11200	—	—	12.545	665-809
SnS	—	—	-8380	—	—	6.728	776-977
SnCl ₄	—	—	-1955	—	—	7.856	m.p.-3000
SiCl ₄	-33	115	-1572	—	—	7.64	273-333
SnCl ₂	247	652	-6350	-5.03	—	24.68	520-952
SeO ₂	subl.	320	-6170	-3.02	—	21.40	298-b.p.
TeO ₂	733	—	-13940	-3.52	—	23.51	298-m.p.
TiCl ₄	-25	137	-2919	-5.788	—	25.129	298-b.p.
Zn	421	906	-6620	-1.255	—	12.34	m.p.-b.p.

SUBJECT INDEX

- Activators in flotation, 33
- Alumina preparation, 338, 399-424
- acid processes, 398
 - alkaline processes, 399
- Bayer process, 397, 400-11
- autoclave, 400
 - digesting treatment, 402-5
 - continuous, 402
 - intermittent, 402
 - economics, 411
 - hydroxide calcination, 408
 - liquor precipitation, 406
 - tanks, 406-7
 - recovery of sodium hydroxide, 409
 - separation of red mud, 406
- Deville-Pechiney process, 411-22
- agitation leaching, 414, 416
 - carbon-dioxide blow, 417
 - carbonation, 417
 - carboniser, 419
 - continuous leaching, 414, 416
 - percolation leaching, 414
 - diffusor, 415
 - from clays and marle, 424
 - from nepheline, 419
 - Kuznetsov-Zhukovsky process, 423
 - Le Chatelier-Morin process (*see* Deville-Pechiney process)
- Alumina properties, 398-99
- Alumina sources,
- alunite, 394
 - bauxite, 394-95
 - cyanite, 394
 - kaolin, 394
 - nepheline, 394, 422
- Aluminium,
- as deoxidiser for Bessemer steels, 95
 - cast alloys, 392
 - historical survey, 396, 397
 - properties, 391, 398-99
 - uses, 393-94
 - wrought alloys, 392
- Aluminium alloy production, 457-64
- electrothermal silumin, 464
 - silicon-aluminium alloys, 463
 - thermal processes, 462-63
- Aluminium metal production, 430-68
- aluminium-reduction cell, 430-31
 - care of cell, 442, 446-52
 - improvements in design, 441-45
 - self-baking continuous anode, 442
 - anode effect, 434
 - theory, 435
 - bath composition, 431-32, 440
 - theory, 432-33
 - bath temperature, 439, 447
 - care of anodes, 448
 - care of electrolyte, 447
 - cryolite preparation (*see* Cryolite preparation)
 - current density, 441
 - electrode manufacture (*see* Carbon products manufacture)
 - electrode spacing, 440, 447
 - electrolytic aluminium casting, 459
 - electrolytic process efficiency, 438, 461-62
 - primary aluminium grades, 453
 - withdrawal of electrolytic aluminium, 448
- Aluminium metal refining, 452-59
- chlorination, 452
 - electrolytic, 455
 - Hoopes (three-layer) process, 456-59
 - magnesium process, 457
 - subcompound method, 459
 - zone recrystallisation method, 459
- Amalgamation of gold, 350, 356-61, 374
- amalgam, 356
 - amalgam distillation, 360-61
 - mill bullion production, 361
 - apron-plate method, 358
 - barrel method, 358
 - inside method, 357
 - outside method, 357-58
- Arc-furnace processes, 124
- acid working, 157
 - economics, 128
 - double refining, 124
 - single refining, 126

- single-slag working, 126
- two-slag working, 124
 - slags, 124-25
 - stages, 125
- Bessemer copper-nickel matte, 212
 - composition, 212
 - refining, 212-13
 - Mond process, 214
 - stages, 213
- Bessemer process,
 - acid, 87
 - charge composition, 89
 - conversion of iron, 89-92
 - converter, 87, 96-7
 - side-blow converter, 97-9
 - theory, 87-9
 - basic, 92
 - charge, 93
 - conversion of iron, 93
 - converter, 93, 96-7
- Bessemer steels, uses, 101-2
- Bismuth removal from lead, 264
- Betterton-Kroll process, 264
- Blast furnace,
 - control, 84-5
 - description, 57-9
 - efficiency, 85-6
 - for nickel smelting, 201-2
 - reactions in iron metallurgy, 71-80
- Blast-furnace gas,
 - composition, 83
- Blast-furnace plant, 64
 - iron handling, 64
 - slag handling, 64
- Blister copper,
 - conversion to, 175-76
 - electrolytic refining, 176, 182-86
 - cells, 182-84
 - current, 186-87
 - electrolyte purification, 189
 - voltage, 186-87
 - fire refining, 177
 - furnaces, 178
 - slags, 181-82
 - stages, 178
- Blowers, for blast furnace, 61
- Blue powder, 261, 327
- Butters filter, 307
- Cadmium
 - extraction from copper-cadmium residue, 344
 - extraction from lead concentrates, 269
- extraction from zinc concentrates, 343-44
- occurrence, 343-44
- reduction in zinc distillation, 327
- recovery in zinc fractional distillation, 340
- Carbon products manufacture,
 - for electrolytic aluminium production, 397, 427-29
- Cathode-zinc melting, 318
 - casting, 318
 - dross control, 318
 - in electric furnace, 318
 - in reverberatory furnace, 318
- Classifiers,
 - Akins, 28
 - cone, 30
 - Dorn, 28
 - hydraulic cyclone, 30
 - wet, 28
- Close circuiting,
 - in ore dressing, 31
- Cobalt,
 - manufacture, 221
 - from nickel ores, 221-24
 - from other ores, 224
- Coke, combustion in blast furnace, 71
- Collectors in flotation, 32
- Comminution of gold ore, 357-58
 - by millers, 357-58
- Complex ores, utilisation, 129
- Concentrate, collective, 31, 33
 - definition, 31
 - selective, 31
- Concentration,
 - definition, 18
 - gravity, 36
 - jigging, 36
 - tabling, 38
- Converter nickel matte refining, 205
 - electric furnace, 205
 - rotary kiln, 204-05
 - roaster, 205
- Copper,
 - alloys, 134-35
 - production, 138
 - pyrometallurgical methods, 138-41
 - slags, 142-46
 - hydrometallurgical methods, 146-48
 - properties, 134
 - secondary, 175
 - resmelting, 175-76
 - sources of primary copper, 136-37
 - tough-pitch, 181

- Copper concentrate,
 - smelting, 163-69
 - electric furnace, 169
 - reverberatory furnace, 163
 - suspension process, 169
- Copper converter, 170
- Copper matte conversion, 170
 - doubling, 173
 - slags, 174
 - waste gases, 174
- Copper matte smelting, 148, 157
 - from concentrates, 157
 - fluidised-bed reactors, 163
 - roasters, 159
 - roasting, 157-63
 - from ores, 148
 - copper-sulphur process, 148, 154-57
 - pyritic process, 148-49
 - semipyrritic process, 148-49
- Copper-nickel matte bessemerising
(see Copper-nickel matte conversion)
- Copper-nickel matte conversion, 212
- Copper recovery from molybdenum ores, 530
- Copper smelting,
 - blast furnace, 148
 - charging, 149, 153-54
 - construction, 148-50
 - slags, 148, 152-53
 - tapping, 148-49, 152-53
 - theory, 151
- Crusher,
 - gyratory, 21
- suspended spindle, 21
 - jaw, 21
 - Symons (cone), 21
- Cryolite, preparation, 424-26
- Cupel, 261
- Cupellation, 261
- Current efficiency, 186, 361-70, 374
- Cyanidation of gold, 350
 - agitation technique, 364
 - batch, 368
 - continuous, 368
 - agitators, 366
 - central-lift type, 366
 - edge-lift type, 367
 - all-sand technique, 364, 374-75
 - all-slime technique, 364, 374-75
 - chemistry, 361-62
 - counter-current decantation, 370
 - percolation leaching, 364, 366
 - vats (tanks), 364
 - series leaching, 369
 - simple decantation, 369
 - single-vat leaching, 365
 - solvents, 362
 - thickening of solution, 369
- Deoxidation,
 - in Bessemer process, 95-6
 - in open-hearth process, 116
- Deoxidisers for Bessemer steels, 95
- Depressors in flotation, 33
- Dewatering, definition, 41
 - drying, 41, 47, 48
 - filtering, 41, 44
 - thickening, 41-42
- Dezincing, 262-64
- Direction of reactions, determination, 19
- Disintegrator for gas cleaning, 70
- Distillation, definition, 17
- Drier, 47
 - rotary kiln, 47
- Doré silver, 259, 261-62
- Duplex processes, 128, 129
- Dust catcher,
 - cyclone, 66
 - dry, 66
 - inertia, 66
- Electric processes, 121
 - arc-resistance, 121-23
 - furnaces, 121
 - induction, 121
 - furnace, 128
- Electrolysis of zinc sulphate solution, 109-16
 - additions, to bath, 315
 - cells, 315-16
 - current efficiency, 313
 - electrochemical reactions, 312
 - energy consumption, 313
 - local-cell action, 314
 - voltage requirements, 313
- Electrolytic lead refining, 267
- Electrolytic nickel refining, 217
 - bath composition, 219
 - anolyte, 219-20
 - catholyte, 221
 - cell, 221
 - electrochemical reactions, 217
- Electrolytic tin refining, 288
- Extraction processes, def., 18
- Filter-presses, 310
- Filters,
 - drum-type, continuous, 44

- rotary disk, 47-8
- vacuum,
 - intermittent, 44
 - Nutsch, 44
- Flotation, def., 32
 - bulk, 34
 - differential, 34
 - selective, 33, 34
 - simple, 34
- Fluxes, in iron metallurgy, 57
- Frothers, in flotation, 32
- Gas cleaning in blast-furnace operation, 66, 69-71
 - dry mechanical, 66
 - electrical precipitation, 68, 71
 - wet mechanical, 67-8
- Germanium, recovery from zinc concentrates, 344-46
- Gold,
 - outline of recovery methods, 349
 - properties, 347
 - sources, 348
- Gold bullion,
 - fineness, 385
 - refining, 385, 387-88
 - chlorination (Miller) process, 385-86
 - dry method, 385-86
 - electrolytic, 385-86
 - wet method, 385-86
- Gold precipitation from cyanide solution, 370-74
 - by cementation, 370
 - with aluminium, 370
 - with zinc, 370
 - chemistry of, 370
 - composition of precipitate, 374
 - zinc-dust precipitation installation, 371-72
- Gold recovery, 374-79
 - energy consumption, 375
 - from antimonial ores, 379
 - from arsenical ores, 379
 - from coaly ores, 379
 - from coppery gold ores, 379
 - from telluride ores, 379
- typical flow sheets, 374
 - criteria for selection, 375
- Gold refining by electrolysis, 387
 - Wohlwill process, 387
- Gravity concentration of gold ore, 351-356, 374
 - hydraulic traps, 355
 - sluice, 351-55
- Hard head, 282
- Hematites, 52
- Hot-blast stoves, 61
- Hydrometallurgy, def., 16
- Indium, recovery from zinc concentrates, 344-46
- Ingot production, 129
 - casting into moulds, 129-30
 - bottom pouring, 130
 - top pouring, 130
 - continuous casting, 133
 - vacuum degassing, 131
- Ion exchange, def., 18
- Ion-exchange resins, 18
 - anionic, 18
 - cationic, 18
- Iridium (*see* Platinum-group metals)
- Iron,
 - crystal transformations, 49, 50
 - effect of impurities, 51
 - lattice structure, 49, 50
 - minerals, 50
 - properties, 49-51
- Iron ores,
 - classification, 52
 - preliminary treatments, 53
- Jigging, def., 36
- Jigs,
 - plunger, 37
 - pulsator, 38, 39
- Kaolin, 396
- Killed steel, Bessemer, 96
- Leaching, def., 17
- Lead,
 - alloys, 226-27
 - commercial grades (table), 249
 - uses, 226
 - properties, 225
 - sources, 227
- Lead blast furnace, 238-40
- Lead bullion improving, 254, 266-67
- Lead bullion refining,
 - alkali-chloride process, 256
 - antimony removal, 253
 - arsenic removal, 254
 - continuous processes, 265-67
 - copper removal, 253-54
 - degolding, 258
 - desilverising, 258

- drosses, 253-54, 261
- pyrometallurgical, 251
- with zinc, 259
- Lead bullion softening (*see* Lead bullion improving)
- Lead concentrates,
 - blast roasting, 233-34
 - composition, 227-28
 - sintering, 233-38
 - double-over, 235
 - single-pass, 235
- Lead mattes,
 - composition, 248
 - recovery from slag, 248
 - forehearth for, 248
- Lead-ore smelting, 230
 - in ore-hearth, 230-32
 - charge for, 231
 - principles, 229-30
- Lead smelting,
 - blast-furnace, 238
 - reduction, 244
 - charge, 244
 - procedure, 244-45
 - slags, 244-45
- Lead-smelting slags, 244-45
 - recovery of matte from, 248
 - re-treatment by fuming, 248
 - furnace for, 249
- Limonites, 52
- Liquation,
 - for removal of lead from silver-zinc dross, 259-61
- Magnesium,
 - production (*see* Magnesium production)
 - properties, 469
 - sources, 470
 - uses, 470
- Magnesium production, 472
 - casting, 494
 - chlorination of magnesium oxide, 475
 - clorinator, 476-78
 - dehydration of source minerals, 472-73, 478
 - electrolyte, 480
 - decomposition voltage, 482
 - electrical conductivity, 480
 - fusibility, 480
 - solubility of magnesium, 483
 - specific gravity, 480
 - surface tension, 483
 - viscosity, 483
 - electrolytic, 472, 479-92
 - bath composition, 483, 489
 - bath temperature, 484, 490
 - current efficiency, 485
 - economics, 495-96
 - magnesium withdrawal, 490
 - slime removal, 491
 - electrolytic cell, 479, 485
 - maintenance, 489
 - refined grades (table), 492
 - refining, 493
 - by fusion with fluxes, 493
 - by retorting, 493-94
 - thermal processes, 482, 496
 - arc-furnace, 496-98
 - calcium-carbide reduction, 502-03
 - carbon reduction, 496-98
 - silicon reduction, 499
 - retort furnace for, 500
- Magnetic separation, *def.*, 39
- Magnetic separators, 40
 - disk, 40
 - drum, 40-41
- Magnetites, 52
- Manganese ores, 52
- Metals,
 - abundance in Earth's crust, 15
 - classification, 11-12
 - definition, 11
 - ferrous, 11
 - minor, 13
 - noble (precious), 12
 - non-ferrous, 11-12
 - heavy, 12
 - light, 12
 - radioactive, 13-14
 - refractory, 13
 - scattered, 13
 - sources, 14, 16
- Metallurgical processes,
 - basis, 18
 - definition, 16
- Middlings, *def.*, 31
- Mill gold bullion, 361
 - refining, 361
- Mills, 23
 - ball, 23
 - beater, 23
 - grinding, 23
 - hammer, 23
 - rod, 23
 - tube, 25
- Molybdenum,
 - concentrates, 522-23
 - conversion, 522-23

- preparation, 522
 - roasting, 523
 - ductile molybdenum manufacture, 528
 - metal powder production, 528
 - properties, 521
 - roasted concentrate breakdown, 523
 - by distillation, 525-27
 - with ammonia, 523-25
 - with caustic soda, 527-28
 - with sodium carbonate, 527-28
 - sources, 522
 - use, 521-22
- Nepheline, 395
- Nickel,
 - alloys, 189
 - concentrate smelting, 207
 - from sulphide ores, 207
 - in blast furnace, 211
 - in electric furnace, 206, 210
 - in reverberatory furnace, 207-10
 - grades, to U.S.S.R. Standard, 218
 - matte, 202-04
 - composition, 202
 - conversion, 202
 - slag, 203
 - production (*see* Nickel Production)
 - properties, 189
 - smelting (*see* Nickel smelting)
 - sources, 192-93
- Nickel production,
 - by hydrometallurgy, 194-95, 197
 - by pyrometallurgy, 195-97
 - from oxide ores, 193, 198
 - from sulphide ores, 195, 206-17
- Nickel smelting,
 - blast-furnace, 199-02
 - charge, 201
 - coke consumption, 202
 - matte composition, 201
 - slag, 201
- Open-hearth furnace,
 - automatic control, 121
- Open-hearth process,
 - acid, 117
 - furnace for, 117
 - basic, 111
 - stages in, 111, 115
 - charge composition, 110
 - cold pig-and-scrap variety, 110
 - economics, 119
 - fuels, 108
 - furnaces, 104-08
 - hot pig-scrap-and-ore variety, 110
 - principles, 102, 103
- Open-hearth steel,
 - acid, 118
 - uses, 118
- Ore,
 - classification, 16
 - comminution, 20
 - classification, 20, 21
 - equipment, 20
 - stages, 20
 - complex, 31
 - definition, 14, 15
 - designation, 14
 - dressing (*see* Ore dressing)
- Ore body, def., 14
- Ore dressing,
 - definition, 16, 17
 - methods, 31, 32
 - scope, 31
- Ore mineral, def., 14
- Osmium (*see* Platinum-group metals)
- Overflow, in classifying, def., 28
- in thickening, 41
- Oxygen enrichment of blast, 86
- in open-hearth process, 119
- Oxygen steel-making,
 - Kaldo process, 101
 - LD process, 100
 - LD-AC process
 - Rotor process, 101
- Palladium (*see* Platinum-group metals)
- Pelletising,
 - in iron metallurgy, 56
 - in lead-ore preparation, 234
- Pig iron,
 - formation in blast furnace, 78
 - grades, 80-2
- Platinum-group metals,
 - alloys, 383
 - processes for recovery, 384, 388
 - properties, 392
 - refining, 388, 390
 - sources, 384
 - uses, 383
- Poling, 178, 181
- Precipitation, def., 17-8
- Pulp,
 - flotation, 32
 - grinding, 23
- Pyrometallurgy, def., 17

- Reaction rate, 19
- Reverberatory furnace for copper concentrate smelting,
 - charge, 166
 - economics, 168-69
 - fuel, 165
 - products, 168-69
 - tapping, 166
- Rhenium, recovery from molybdenum ores, 530
- Rhodium (*see* Platinum-group metals)
- Rich lead, 261-62
- Rimming steel,
 - Bessemer, 96
 - open-hearth, 116-17
- Roasting, *def.*, 17
- Rolls, 23
- Ruthenium (*see* Platinum-group metals)
- Sands,
 - in classifying, 28
 - in gold recovery, 364
- Scrap zinc recovery, 341
 - by reductions smelting, 342
 - by Waelz process, 341
 - charge, 342
 - kiln, 342
 - slag, 342
 - values in slag, 342
- Screens,
 - bar, 27
 - cylinder, 27
 - revolving, 27
 - vibrating, 27
- Silver,
 - production, 381
 - properties, 380
 - secondary, 381
 - sources, 381
 - uses, 380
- Silver refining,
 - by electrolysis, 386
 - Moebius process, 386-87
- Silver-zinc dross, 259
 - dezincing by distillation, 261
 - removal of lead from, 259-61
- Sintering,
 - definition, 17
 - in iron metallurgy, 53-56
 - in nickel production, 199
 - travelling-grate machine, 55-6
- Sizing,
 - definition, 26
 - screen, 27-8
- Slag in blast furnace,
 - composition, 82
 - formation, 79
- Smelting, *def.*, 17
- Spray scrubbers,
 - rotary, 70
 - static, 70
- Standard affinity, 19
- Standard free energy, 19
- Sulphur, effect on blast-furnace operation, 80
- Surfactants in flotation, 32
- Table concentration, 38
- Tailings, *def.*, 31
- Thallium, recovery from zinc concentrates, 344-46
- Thickeners, 42-4
- Tin,
 - alloys, 270-71
 - extraction from concentrates, 275
 - grades (table), 283
 - ores (*see* Tin ores)
 - properties, 270
 - refining, (*see* Tin refining)
 - smelting (*see* Tin smelting)
- Tin ores,
 - extraction of other metals, 289
 - preparation for smelting, 281
 - by leaching, 273-75
 - autoclave for, 273
 - by roasting, 272
- Tin refining,
 - by drossing, 286
 - by liquation, 284
 - elimination of antimony, 286
 - elimination of arsenic, 286
 - elimination, of iron, 286
 - methods, 283
 - removal of bismuth, 287
 - removal of lead, 284-87
 - by chloridising, 287
- Tin smelting,
 - chloridising process, 276
 - primary, 277
 - in electric furnace, 281
 - in reverberatory furnace, 278-79
 - charge for, 279
 - reduction process, 275-77
 - slag re-smelting, 282-83
- Titanium,
 - concentrate treatment, 533
 - metal production, 536
 - chlorinator, 534

- Kroll process, 536
- properties, 531
- sources, 532-33
- sponge, 539
 - arc-melting, 539
 - iodide-process, 539-41
 - powder-metallurgy treatment, 539
- Tungsten,
 - concentrate treatment, 507-08
 - manufacture of ductile tungsten, 517
 - production of tungstic acid, 510-11
 - production of tungsten metal powder, 515
 - properties, 504
 - sources, 506
 - uses, 505
- Underflow in thickening, 41-2
- Work lead, 259
- Zinc,
 - concentrates (*see* Zinc concentrates)
 - distillation (*see* Zinc distillation)
 - grades (table), 335
 - ores, 291
 - refining (*see* Zinc refining)
 - principles of extraction, 292
 - production by electrolysis (*see* Zinc hydrometallurgy)
 - properties, 290
 - smelting in blast furnace, 333-35
 - uses, 291
- Zinc concentrates,
 - leaching, 301-08
 - acid, 302, 306-08
 - air-operated leaching tank, 303
 - Butters filter, 307
 - continuous, 303
 - double, 302
 - equipment, 303
 - iron purification, 301
 - mechanically agitated tank, 303
 - neutral, 302, 306-07
 - Pachuka tank, 303
 - roasting, 294
 - fluid-bed process, 298-301
 - reactor, 298-99
 - suspension process, 295-96
 - furnace, 296-97
- Zinc distillation, 292-332
 - effect of impurities, 326-27
 - electric furnace, 332
 - retort processes, 321-32
 - horizontal, 321
 - charge composition, 321
 - condenser, 321
 - furnace, 323
 - preheaters, 323
 - retorts, 321
 - vertical, 330-32
 - plant, 330
 - retorts, 330, 332
 - products, 329-30
 - re-treatment, 329-30
 - roasting prior to, 324
- Zinc hydrometallurgy,
 - economics, 319
 - high-density working, 320
 - low-density working, 321
 - sulphate solution, 308-11
 - composition, 309
 - copper purification, 311
 - electrolysis, 311
 - purification, 308-09
 - removal
 - of cadmium, 309
 - of chlorine, 311
 - of cobalt, 308
 - of copper, 309
- Zinc refining,
 - by redistillation (fractional distillation), 335-37
 - apparatus, 339
 - by liquation, 336-37
 - electrolytic, 336

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